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Report 50

Division of Mines

PLANTS AS A GUIDE TO MINERALIZATION

By DONALD CARLISLE and GEORGE B. CLEVELAND

Price 50¢

PLANTS AS GUIDE TO MINERALIZATION †

By Donald Carlisle * and George B. Cleveland **

OUTLINE OF REPORT

ABSTRACT

buried ore deposit may provide to the soil above abnormal amount of the metal or metals it contains; urn, the soil may provide a large amount of the same als to the plant cover. The ore deposit may therefore, er favorable conditions, be detected by the abnor- ly high concentration of these metals in the plants, py the distribution of plants that will or will not rate certain metals more readily than others. If the ts are systematically collected and carefully ana- d, the results may indicate the possibility of a buried deposit. This technique of sampling, analyzing, and rpreting the plant cover is called biogeochemical specting.

lthough the method has the advantage of rapidity is relatively inexpensive, the numerous factors (such ge and organ of the plant, soil pH, geochemistry of and its exchange capacity) that bear on the concen- ion of metals within plants must be considered. onomists and other research workers have provided e data; biogeochemical field work has added more.

hree known molybdenum deposits in California were spected in the course of this study. At the Bour ybdenum mine, San Diego County, molybdenite is eminated as flakes in an aplite dike that cuts grano-

diorite. Plants growing above the dike showed an abnormally high concentration of molybdenum; the soil in which they were rooted was also high in molybdenum, but not so anomalously as the plants.

Flakes of molybdenite were found in the Cosumnes mine, El Dorado County, along the contact of an igneous body and metasedimentary rocks of the Carboniferous (?) Calaveras group, though the mine itself was not primarily worked for molybdenum. Plant samples from the area showed the highest concentration of molybdenum to be over the contact zone, as geological field studies also indicated.

At the Tyler Creek tungsten mine, Tulare County, the analysis of samples collected along a fault zone that traversed several rock types indicated that the underlying rock type exercised some control over the molybdenum concentration. No definite pattern of mineralization could be determined from the plant analysis; higher values were seemingly distributed at random.

Several factors other than the metal content of the soil may influence the metal content of a plant. If these factors vary within the area of survey, and if they have a significant effect on metal uptake, the biogeochemical results are misleading. Soil moisture and drainage influence the availability of some metals although, in general, the influence of the physical properties of soil is probably not great. Even the amount of sunlight and shade has a slight effect for some plants. The largest effects, however, are associated with the chemical properties of the soil both as an influence on the metabolism of plants and as a control of the state of the metal in the soil, as most of the metal in the soil is present not in minerals or in solution but as ions sorbed or exchanged in the soil materials, especially on clay minerals and organic matter, or else as complex ions. Consequently, the ability of the plant to absorb metals is moderately to profoundly influenced by the kind and concentration of exchange materials, by the soil pH, by the kind and concentration of other ions, and by organic materials and micro-organisms. The exchange capacity of a soil also largely determines the amount of metal that will be taken and retained from various sources. Available data suggest that the clay or organic content of a soil can be responsible for variations of a few fold in the metal content of that soil.

BIOGEOCHEMICAL PROSPECTING

Biogeochemical prospecting, like most geochemical and geophysical methods of exploration, is an adjunct to other techniques for the discovery of economic mineral deposits. As with other geochemical and geophysical methods, clues to the location of hidden deposits are sought through relatively inexpensive procedures performed on readily accessible materials at the earth's surface. In biogeochemical prospecting the procedures are (1) the observation of the distribution of plants (indicator plants) that tolerate or fail to tolerate abnormally high concentrations of certain metals in the soil (this method is sometimes called botanical prospecting); or (2) the sampling and analysis of plants that concentrate or of plants that merely acquire certain metals
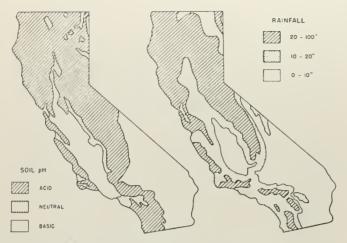
FIGURE 1. Maps of California showing the close relationship between soil pH and amount of rainfall. *Modified from Jenny (1951).*

from the soil, (accumulator plants)* and (3) the interpretation of the data thus obtained. The basic assumptions, then, are that a high metal content in the soil may reflect a deposit of metal somewhere at depth and that the high metal content in the soil may be reflected in some way in the plants. Indicator plants, though of limited occurrence, are very useful when present and offer an extremely cheap method for reconnaissance of large areas to show variations in metal content of the soil. An example is the use of some species of *Astragalus, Stanleya,* and other selenium- and sulfur-tolerant plants in the search for uranium deposits (Cannon, 1952; Cannon and Starrett, 1956; Dorn, 1937; Lidgey, 1897; Hawkes, 1950). The second technique, systematic sampling and analysis of plants for their metal content is more widely applicable, though best suited to small areas. It is with this technique and some of the problems involved that this report is concerned. The term biogeochemical prospecting will be used for this second technique.

Unusually high concentrations of metal commonly do develop in the soil near ore deposits. For example, the metal in the soil may be the residuum of a metal deposit now eroded. Grains of a primary ore mineral may have persisted through the weathering process or may have been concentrated through removal of more easily weathered gangue minerals. Residual concentrations of cassiterite, gold, and other minerals are sometimes produced in this way. If the primary ore mineral weathers readily a secondary mineral such as azurite, malchite, cerrusite or garnierite may remain in the soil. Under still other circumstances only traces of the ore metal may remain as a contaminant but in concentrations sufficiently large to distinguish the soil from other soils nearby. Or the metal in the soil may have been introduced or dispersed either as solid mineral particles carried by water, wind, or ice, or as dissolved ions in ground waters. In this event the source of the metal might not be nearby but might nevertheless be discovered

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* The use of the term accumulator plant for all plants that can be sampled for a given metal is misleading. Many plants used successfully by biogeochemists contain lesser concentrations of the metal sought than does the underlying soil. The plants sample the soil but they do not necessarily accumulate the metal.

through careful study of the dispersion pattern [t ?]pears also that metal ions are able to migrate s[?]fa ward directly from hidden deposits by proces[s ?] well understood. Presumably they travel in pa[?] upward percolating ground water and in part [?] fusion within ground water. Ion exchange an[d ?]ot reactions with soil materials probably play a rol[?]On within the reach of plant roots, metals may be [?]th concentrated at the surface very effectively by [?]la themselves. Goldschmidt (1937, pp. 670-71) has [?]in out how absorption of metals by plant roots, tra[?]lo tion to the upper organs of the plant, and return [?] earth when leaves are shed or the plant dies tend [?] centrate them in the upper layers of the soil.

Agronomists have long recognized the ability of [?]la to accumulate some metals from the soil, especiall[?]th metals useful or necessary to the plant and als[?]th ability to absorb other metals present in the so[?]e though these appear to serve no useful purpose [?] plant. Probably every element could be found in [?]la if sensitive enough analytical techniques were use[d ?]Ev the synthetic element, plutonium, is absorbed and [?]ra located within plants (Jacobson and Overstreet, [?]4s In some cases an unusually large amount of [?] metal in the plant can be correlated with an un[?]a high concentration of the metal in the soil in wh[?]t plant is growing. The abnormal amounts of go[?]a copper reported in horsetails is a classic example ['?]ra analyses of many of the world's coals did m[?]h prompt an early interest in the relationship b[?]we plant cover and the subsurface geology. Milner [?]92 reported vanadium from Scottish coal and gol[?]fr coals at Cambria, Wyoming. Germanium has been [?]u in many of the world's coals by Goldschmidt (193[?]a more recently by others (Stadnichenko et al., 195[?]T work of Palmquist and Brundin reported by the S[?]d Prospecting Company in 1939 was among the first [?]a cal applications of biogeochemical principles. Th[?]n method was employed with some success by Rank[?]a the vicinity of the nickel ore deposits at Nev[?]b northern Finland (Rankama, 1940). The value [?] geochemistry was demonstrated by many investiga[?]rs Scandinavia and has been applied successfully i[n ?]Gr land, Greece, U. S. S. R., Spain, Australia, South [?]ri Nigeria, Canada, Venezuela, Poland, Brazil, Ge[?]a and the United States.

Prospecting Procedure. The procedure for [?]g chemical prospecting in an area is as follows: [?]le samples are collected according to a grid patter[n ?]r intervals along traverses. The same species of pla[?] same organ of the plant and if possible plants [?] same age are sampled at each station. Some worke[r ?]p fer to use only twigs of the previous year's g[?]w others use only leaves. Sampling stations may be f[?]u feet to 1000 feet apart depending upon the expect[?]s of the target and the size of the area involved[?]It general practice to collect a compound sample fo[r ?]e station by gathering the leaves, twigs or whatever [?]g is sampled from two, three or four trees or plants [?]re ing within a radius of perhaps 5 to 25 feet of the s[?]th All sampling is done within a single day or a fev[?]la

Where no single plant species grows over the [?]b area some workers have sampled two kinds of pl[?]ts

aempt to establish a correlation in metal uptake
⋯n them through sampling both plants together at
⋯l locations. Usually, though, geological considera-
⋯sor the distribution of already known deposits
⋯t the size of the area to be sampled and a single
⋯e plant species can be found throughout.
⋯ purpose of an investigation dictates, in most in-
⋯s, the number of samples to be collected. If the
⋯on of a known ore body is the object of an in-
⋯ation, perhaps then fewer samples will be required
⋯ieve the objective than if a totally unknown area
⋯g investigated. In the former case the general
⋯e of the ore body affords a starting place from
⋯ traverses can radiate. Moreover, if the deposit has
⋯ur trend the problem is narrowed to sampling the
⋯eyond the extremities. If the area is entirely un-
⋯ it is necessary to sample quite intensively. In
⋯l a widely spaced grid pattern will give, at the
⋯ of a program, some indication of where the favor-
⋯ocalities lie. After this preliminary attempt, de-
⋯work in likely areas may establish the limits of a
⋯t. Various means have been employed to collect
⋯m samples such as the leaf punch, which cuts out
⋯ area of plant material, but this technique fails to
⋯nto account the variable thickness of the leaf.
⋯s, cutters and other garden devices have all been
⋯ut none with any particular advantage. The type
⋯ting tool to use is best left up to the individual and
⋯ the metal from which it is made contributes to the
⋯nination of a sample, little concern need be given
⋯hase of the operation.
⋯ood deal of attention has to be given to the
⋯rs of contamination. Plants can become contami-
⋯ in two important ways before they are sampled.
⋯ been demonstrated that wind blown material from
⋯s and smelters poses a serious problem in some
⋯ and soil contamination through rain-spattering
⋯nstant hazard when plants are sampled too close
⋯ surface of the ground. In areas where contamina-
⋯ likely, organs such as twigs should be sampled in
⋯rence to leaves, because the ratio of total contami-
⋯area to the volume of the organ is much less in
⋯se of twigs than in the case of leaves. If there is
⋯oubt as to whether a sample is contaminated or
⋯ can be carefully washed in a dilute solution of
⋯chloric acid. This procedure will be sufficient in
⋯cases to remove contaminants. Some prospectors
⋯e bark from twigs to remove surficial dust. Others
⋯ wash the samples in distilled water with or with-
⋯ detergent. Lest this phase of the operation be
⋯too lightly, it has been demonstrated that the
⋯t of metal picked up by the hand from turning a
⋯doorknob is sufficient to produce a positive metal
⋯n with the reagent dithizone.
⋯plant samples are taken to the laboratory in
⋯paper bags where they are dried and ashed under
⋯rd conditions. Since the metal content is usually
⋯ated in terms of the ash weight (agronomists com-
⋯use "dry weight") and since the weight of "ash"
⋯ced from a given amount of dried plant depends
⋯ the length of time and the intensity of heating
⋯specially important that this procedure be stand-
⋯d. Ashing temperatures above 450° centigrade may
⋯volatilization of some elements. The ash is weighed

and analysed for the metal sought by one of several
techniques. Rapid, accurate wet chemical procedures
have been developed for zinc, copper, "heavy metals,"
molybdenum, uranium, and nickel. Spectrographic
analysis is sometimes used where the equipment is avail-
able. It provides a permanent record, has a high degree
of sensitivity, and can analyze for several elements at
once.

Contamination is a serious problem at this stage also.
It has been suggested that the high concentration of
lead and other metals in wall paints, for example, makes
them important sources of error where uncovered
samples are placed near old flaking paint.

The analyses, usually reported as parts per million
(ppm) of metal in the plant ash, are plotted on a map
and interpretations may then be made for areas of
possible mineralization.

The technique is thought to have some advantages
and some disadvantages as compared with analysis of
soils directly for their metal content or with other pros-
pecting techniques.

Advantages

(1) The metal content of several plants at each station is likely
to be a more representative sample of the area than is the metal
content of a few grams of soil. The plant roots themselves sample
a large volume of soil.

(2) Sampling is rapid and easily done, and is therefore, inex-
pensive.

(3) Plant roots have access to large amounts of soil well below
the surface. This can be an important factor because the concentra-
tion of the metal near the surface of a soil may tend to correlate
with purely surficial conditions and be unrelated to the concentra-
tions deeper in the soil. Moreover the migration of metals in soil
can be extremely slow. Lundblad et al. (1949) have shown, for
example, that of the copper supplied in large amount (250 Kgm
per hectare) to the surface of a peaty copper deficient soil, only
2 percent had penetrated to a depth 5 centimeters below the soil
surface 6 years after application. Most of the copper was fixed in
the upper peaty layers. Nevertheless crops grown thereon did take
up copper.

(4) If plants do accumulate metal concentrations greater than
those present in the soil the analysis of plants may be simpler than
direct analysis of the soil. Usually this is not a major factor.

Disadvantages

(1) The added step of ashing the plant for analysis is not
required in soil analysis unless organic matter interferes with the
analytical procedure.

(2) The unknown influences of many complex and many un-
known factors in addition to metal content of the soil that affect
the uptake and storage of metals by plants.

The more important known factors will be discussed below and
an attempt will be made to estimate whether such factors are
likely to produce variations in the metal content of plants so large
that under some natural conditions they may obscure the varia-
tions in metal content in the soil. It should be pointed out, how-
ever, that soil analysis itself is not free of such complications.
Surficial soil can be enriched in metal though the accumulation
of plant debris, "Goldschmidt enrichment"; and is therefore sub-
ject also to the complications of plant metabolism. According to
Mitchell (1955, p. 269-70), Goldschmidt enrichment appears to
apply to Scottish moorland soils, on an ignition weight basis, for
Ag, Cu, Mo, Pb, Sn, and Zn, but not for Co, Ni, Cr, V, Mn, Ti,
Ga, Li, Rb, Ba or Sr. The effect is strongest where the metal
enters into insoluble combinations with organic or inorganic ma-
terials. In addition the metal content of surficial soil may be in
large part dependent upon the abundance of soil materials that
are capable of selectively absorbing and binding or fixing metal
ions. Micro-organisms in the soil commonly are major factors in
controlling metal mobility in the soil. Inasmuch as direct soil
analysis has become a standard adjunct to other exploration tech-
niques in many places, and since the results obtained may depend
in large part upon biological enrichment of the upper layers of the
soil, it is desirable that geologists and others involved in this work

SAMPLER PLANTS FOR BIOGEOCHEMICAL PROSPECTING †

Common	Scientific	Cu	Zn	Al	Se	Hg	Ge	Fe	Au	B	U	Mn	Ni	Mo	Ag	Sn	W	V	Sr	Co	Mg	Ba	
Green alder	Alnus sinuata	x	x					x				x											
Willow	Salix sp.	x	x							x		x											
Scrub oak	Quercus tubinella	x																					
Emory oak	Quercus emoryi	x																					
Mountain mahogany	Cercocarpus ledifolius		x																				
Mountain hemlock	Tsuga mertensiana	x	x																				
Balsam fir	Abies amabilis	x	x																				
Giant cedar	Thuya plicata		x																				
Lodgepole pine	Pinus contorta	x	x					x	x	x		x			x								
Black cottonwood	Populus trichocarpa	x	x					x		x		x											
Larch	Larix occidentalis	x	x							x		x											
Aspen	Populus tremuloides	x	x					x	x	x		x			x								
Soolpolallie	Shepherdia canadensis		x							x		x											
Douglas fir	Pseudotsuga taxifolia	x	x					x	x			x			x								
Western red cedar	Thuja plicata	x	x					x				x											
Western hemlock	Tsuga heterophylla	x	x					x				x											
Rocky mountain juniper	Juniperus scopularum	x	x																				
Juniper	Juniperus sp.							x			x	x											
Pinyon pine	Pinus monophylla										x												
Ponderosa pine	Pinus ponderosa	x	x					x				x			x								
White bark pine	Pinus albicaulis	x	x																				
Englemann spruce	Picea engelmanni	x	x					x				x											
Sitka spruce	Picea sitchensis	x	x																				
White spruce	Picea glacua	x	x					x				x											
Dwarf juniper	Juniperus communis	x	x						x						x								
Rocky mountain fir	Abies lasiocarpa	x	x						x						x								
Scrub birch	Betula glandulosa	x	x																				
Mountain birch	Betula occidentalis	x	x																				
Silver birch	Betula popyrifera	x	x																				
Syringa orange	Philadelphus lewisii	x	x																				
Mountain maple	Acer glabrum	x	x					x				x											
Apple			x																					
Poplar	Populus grandidintata		x																					
Western red birch	Betula fontinalis							x				x											
Grand fir	Abies grandis							x				x											
Willow	Salix scouleriana							x				x											
Red alder	Alnus rubra							x				x											
Broad leaf maple	Acer macrophyllum							x				x											
Vine maple	Acer circinatum							x				x											
Citrus								x													x		
Choke cherry	Prunus demissa	x	x																				
Flowering dogwood	Cornus nuttallii							x				x											
Sumac	Rhus typhina		x																				
	Sassafras variifolium		x																				
Soft maple	Acer saccharinum		x																				
Pignut	Carya cordiformis		x																				
	Carya ovalis obvalis		x																				
Hickory	Carya ovata		x																				
Flowering dogwood	Cornus florida		x																				
Black walnut	Juglans nigra		x																				
Red cedar	Juniperus virginiana		x																				
Osage orange	Maclura pomifera		x																				
Sycamore	Platanus occidentalis		x																				
Black cherry	Prunus serotina		x																				
White oak	Quercus alba		x																				
Red oak	Quercus borealis maximus		x																				
Bur oak	Quercus macrocarpa		x																				
Blackjack oak	Quercus marilandica		x																				
	Quercus muhlenbergii		x																				
Pin oak	Quercus palustris		x																				
Post oak	Quercus stellata		x																				
Black oak	Quercus velutina		x																				
Sumac	Rhus copallina		x																				
Black locust	Robinia pseudoacacia		x																				
Nces	Sassafras albidum		x																				
Winged elm	Ulmus alata		x																				
American elm	Ulmus americana		x																				
Slippery elm	Ulmus fulva		x																				
Pine																		x					
Hickory								x				x									x		
Sugar maple	Acer saccharum																						
Princess pine	Lycopodium fabelliforme			x																			
Pecan																							
Brazil nut																							x
Chestnut																							
Oak	Quercus wislizeni														x							x	x
	Pseudotsuga douglasii																						x
	Afzelia africana		x												x								
	Rubiacaea sp.		x												x								
	Bahia nitida		x												x								
	Parinari curatellifolia		x												x								
	Albizzia zygia		x												x								
	Lophira alata		x												x								
	Vitex cuneata		x												x								
	Parkia oliveri		x												x								
	Millettia sp.		x												x								
	Newbouldia lavis		x												x								
	Trichilia prievriana		x												x								
	Anacardiaceae sp.		x												x								
	Sp. indet		x												x								

SAMPLER PLANTS FOR BIOGEOCHEMICAL PROSPECTING—Continued

Common	Scientific	Cu	Zn	Al	Se	Hg	Ge	Fe	Au	B	U	Mn	Ni	Mo	Ag	Sn	W	V	Sr	Co	Mg	Ba	Pb	RE
ak	Quercus douglasii													x										
ush	Artemisia tridentata							x				x												
uckleberry	Gaultheria shallon							x				x												
ckinnick	Vaccinium parvifolium							x				x												
box	Arctostaphylos uva-ursa							x				x												
	Pachystima myrsinites							x				x												
erry	Corylus californica							x				x												
club	Vaccinium sp.	x	x																					
en	Echinopanax horridus	x	x																					
spray	Pteridium aquilinum	x	x																					
ite	Holodiscus discolor	x	x																					
etch	Prosopis juliflora	x																						
ricegrass	Astragalus sp.				x																			
ale	Oryzopsis hymenoides				x																			
	Atriplex confertifolia				x																			
	Vaccinium vitis idaea	x	x											x										
ails	Ledum palustre	x	x											x										
	Equisetum sp.								x						x									
erry	Vaccinium ovalifolium	x	x																					
ush	Symphoricarpos racemosus	x	x																					
	Artemisia trifida	x	x																					
	Viola calaminaria*		x																					
	Thlaspi calaminaria*		x																					
	Amorphia canascens*																						x	
	Viola tricolor*		x																					
	Thlaspi alpestre*		x																					
	Asparagus officinalis		x																					
and eggs	Linaria vulgaris		x																					
over			x																					
	Zea mays		x																					
	Euphorbia maculata		x																					
rod	Solidago sp.		x																					
ail	Equisetum arvense		x																					
	Lobelia inflata		x																					
	Lobelia syphillitica		x																					
in	Plantago lanciolata		x																					
	Pycnanthemum flexuosa		x																					
ed	Ambrosia artemisiifolia		x																					
ush	Amelanchier canadensis		x																					
on seal	Smilacina racemosa		x																					
	Tomanthera auriculata		x																					
	Viola sagittata		x																					
arrot	Daucus carota		x																					
v	Achillea millefolium		x																					
cherry	Physalis sp.		x																					
erry	Celtis occidentalis		x																					
weed	Persicaria hydropiper		x																					
ed	Ambrosia coronopifolia		x																					
ed	Ambrosia elatior		x																					
ragweed	Ambrosia trifida		x																					
uestem	Andropogon furcatus		x																					
bluestem	Andropogon scoparius		x																					
ne	Apocynum sibiricum		x																					
ed	Gnaphalium obtusifolium		x																					
wer	Helianthus mollis		x																					
	Liatrus aspera		x																					
	Desmodium sessilifolium		x																					
eed	Phytolacca decandra		x																					
	Salvia pitcheri		x																					
grass	Sorghastrum nutans		x																					
ush	Symphoricarpos orbiculatus		x																					
	Tridens flavis		x																					
eed	Vernonia interior		x																					
oon	Amelanchier alnifolia	x	x																					
																		x						
																		x						
																		x						
	Calluna rulgaris													x										
leaf					x																			
oss					x																			
w beauty					x																			
					x																			
					x																			
clover																					x			
clover										x														
	Polycarpia spirostyles	x																						
	Thymus serpyllum	x																						
	Viola hirto	x																						
co												x												
aster														x										
paint brush														x										
pea														x										
	Astragalus racemosus				x																			
	Oonopsis condensata				x																			
	Astragalus bisulcatus				x																			
	Xylorhiza parri				x																			
	Astragalus pectinatus				x																			
	Astragalus grayii				x																			
	Aplopappus fromantii				x																			

SAMPLER PLANTS FOR BIOGEOCHEMICAL PROSPECTING—Continued

Common	Scientific	Cu	Zn	Al	Se	Hg	Ge	Fe	Au	B	U	Mn	Ni	Mo	Ag	Sn	W	V	Sr	Co	Mg	Ba
	Stanleya pinnata_____				x																	
	Gutierrezia sarothrae_____				x																	
Dandelion_____	_____	x																				
	Arctostaphylos viscida_____																					x
	Adenostoma fasciculatum_____																					x
	Vivia americana_____													x								
	Medicagohispida_____													x								
	Lotus corniculatus_____													x								
	Trifolium repens_____													x								
	Trifolium fragiferum_____													x								
	Trifolium subterraneum_____													x								
	Melilotus alba_____													x								
	Melilotus indica_____													x								
	Melilotus sativa_____													x								
	Triticum vulgare_____													x								
	Avena sativa_____													x								
	Hordeum vulgare_____													x								
	Chloris gayana_____													x								
	Lolium perenne_____													x								
Rothrock gramma grass_____	Bautiloua rothrockii*_____	x																				
California poppy_____	Eschscholtzia mexicana*_____	x																				
	Holostium umbellatum_____					x																
	Viscaria alpina*_____	x																				
	Melandrium dioecum*_____	x																				
Carnation_____	Polycarpaie spirostylus*_____	x																				
Wild rose_____	Rosa woodsi*_____	x																				
Horsetail_____	Equisetum variegatum*_____	x							x													
Bush cinquefoil_____	Dasiphara fruticosa*_____	x																				
	Cneoridium dumosum_____													x								

† Compiled from various published and unpublished sources.

have some knowledge of the main factors influencing the uptake and storage of metals by plants.

Present Status of the Method

Elements that have been successfully detected by biogeochemical methods are: zinc, copper, lead, tin, tungsten, molybdenum, nickel, chromium, uranium, beryllium, manganese, gallium, strontium, silver, barium, mercury, cobalt, titanium, iron, and gold. A review of the agricultural data shows that aluminum, arsenic, silicon, selenium, germanium, boron, lithium, vanadium, iodine, magnesium, and the rare earths are known to accumulate in plants and therefore can be detected by biogeochemical means.

The accompanying table lists plants that have been successfully used in biogeochemical studies and others that, according to the agricultural data, probably could be used. The table includes both indicator and accumulator plants although the indicators represent only 8 percent of the total. Further, the table shows the dominant use of trees over all plants except that there are no indicators represented among the trees.

Previous Work. The areas in which biogeochemical studies have been conducted are many and diverse. The greatest activity has centered in North America, principally in Canada, with much of the work being done by the University of British Columbia and the Canadian mining industry. Pioneer work in the United States has been led by the U. S. Geological Survey. European contributions have come from Finland and Sweden. Russia has undoubtedly done considerable work in this field in an effort to develop her industrial potential.

The number of commercial organizations using geochemical prospecting in their exploration programs is unknown but apparently very large. Soil sampling and analysis is more popular than biogeochemistry and has become a standard prospecting technique for many private groups in Canada and in the United States. The U. S. Geological Survey, as well as several universities,

is actively engaged in the development and imp___ ment of geochemical techniques.

The U. S. Geological Survey has developed quick water, and plant tests for various metals that ca performed in the field. Recently the Survey has us portable grating spectrograph mounted on a two truck. Geochemical programs have been carried ou at least ten major mining districts and in the dev ment of uranium exploration in the southwest. have been developed for the detection of zinc, ni uranium, and molybdenum in plants. These tests designed to give plus or minus 30-50 percent accu at the minimum rate of 24 to 30 samples per man Under favorable conditions this figure can be raise 60 or as many as 80 determinations per man-day. Survey has also conducted basic research in plant metal relationships in an effort to expand the us ness of biogeochemistry.

The University of British Columbia, with the coop tion of the Canadian mining industry, has perfe various analytical testing techniques using dithizor an indicator for heavy metals. Some 5,000 separate alyses have been run on plant samples to detect an lous concentrations of copper, zinc, lead, molybde iron, manganese, silver, and gold.

On the Colorado Plateau trees growing in sedimen formations have yielded samples indicating that ura may be concentrated at a depth as great as 60 feet (non, 1953); the results of Canadian studies mineralization can be detected through 50 feet of gl drift or 60 feet of muskeg swamp (Webb, 1953, p.

The successful applications of biogeochemical pecting fall into two groups: studies over known bodies and the actual location of new ore deposits the former case the record is marked by varying deg of success. The work of Webb and Millman, Vogt, baugh and others in some cases has shown a less clear cut support of biogeochemical principles. on the other hand Warren and Delavault, Soko

i, Hawks, Rankama and many more have achieved
icant success in their investigations. The great ma-
f of evidence cited in the literature supports the
ses on which biogeochemical prospecting is based,
gh undoubtedly there have been a great many un-
ssful attempts not reported in the literature.

pical examples of successful applications over
n ore deposits are found in the work of Warren
Iawatson (1947) on copper and zinc mineralization
nada. Studies were made in several copper camps
extensive mining operations had definitely out-
positive and negative areas. Tree samples were
lsed and the results between positive and negative
a were compared. In one area five different tree types
owed marked variation in copper concentration
en the mineralized and nonmineralized areas; one
s differed nearly a hundred fold in concentration
the smallest variation was threefold. The average
r concentration for all five trees in the positive
was 13,080 ppm copper as opposed to 560 ppm
r in the negative area.

geochemistry has played an essential role in lo-
small bodies of uranium (Cannon, 1953), vana-
(Cannon, 1953), and iron, and chromium (Buck,
. This method has also been successful in locating
d, pinched, and otherwise hidden extensions of
n ore bodies. A number of near-commercial de-
, such as the chalcopyrite mineralization in the
roo mining district of South Australia, have been
(Harbaugh and Starrett, p. 32, 1953; Webb, p.
953). Cannon and Starrett (1956) have combined
se of plants as indicators and as samplers for
um.

ile the discoveries of new ore are not as spectacular
e might expect from the success of empirical
es, it has been stated that they more than paid for
ntire cost of all exploratory and experimental work
within the last several years (Webb, p. 344, 1953).
the other hand the results from biogeochemical
ecting have not been uniformly reliable. Anoma-
variations in the metal content of plants have been
l which are so haphazard in their distribution that
could not be used safely to plan more expensive
rface exploration. The uptake of some minor ele-
s is not necessarily proportional to their relative
nts in the soils.

ABSORPTION OF METALS BY PLANTS

ants obtain mineral salts from the soil by (1) ion
lt accumulation, (2) ionic exchange, (3) chemical
ination, and (4) by diffusion. The absorption
ss is highly selective, some cations, anions and
cules being effectively accumulated while others are
ded to a remarkable degree. Ion accumulation is
process by which ions may accumulate in much
ter concentrations within the plant cells than the
entration of the same ion in the medium surround-
he plant. This is an energy-expending process tak-
place largely in young growing cells especially near
tips and continuing only while oxygen supply and
erature are conducive to aerobic respiration in the
t. Since aerobic respiration is dependent in turn
the supply of carbohydrates and other organic
rials produced by photosynthesis in the upper or-

gans of the plant, the rate of ion accumulation tends
to fall with any conditions that reduce markedly the
rate of photosynthesis. Ion accumulation may tend to
vary also with the rate of transpiration by the plant and
in addition, ions of one species may have an effect upon
the uptake of ions of other species.

Ionic exchange mechanisms permit the exchange of
anions or cations from the root surfaces of the plant
for anions or cations in the soil. Ionic exchange is prob-
ably not a metabolic process, does not require expendi-
ture of energy by the plant and occurs independently
of aeration or temperature. Carbonic acid or possibly
organic acids produced by the roots and absorbed on the
root surfaces releases hydrogen ions which then may be
exchanged for other cations in the soil fluid or those
sorbed on soil materials. Entry of ions by combination
is similar to their entry by ion exchange. In this process,
however, the ion may become a part of a metal-organic
complex. Iron and magnesium are so absorbed; copper,
zinc, manganese, molybdenum, cobalt and aluminum
may enter such compounds, though knowledge of this
process is very limited.

Simple diffusion from soil to plant is not now thought
to be an important primary process for mineral salt as-
similation though it may contribute in some favorable
circumstances. Nor do mineral nutrients merely travel
along with the water absorbed. Diffusion plays an im-
portant role in the soil quite outside the plant and assists
in the translocation of ions once they have entered the
plant.

Thus the amount of metal taken up from the soil by
a plant is influenced by factors that control the health
and metabolism of the plant and also by many factors
that control the availability of metal ions to the plant.
If these factors vary markedly along a sample traverse
in a biogeochemical survey, or if they vary throughout
the area sampled, the analyses of the plant samples will
reflect these factors as well as, or perhaps to the exclu-
sion of, variations in metal content of the soil. Pre-
sumably, then, these factors might produce misleading
anomalies in plant metal content, suggesting a concen-
tration of metal in the soil that does not exist. Or they
may mask a real concentration of metal in the soil above
a metal deposit. On the other hand, the effect of some
of them may be slight in comparison with the variation
observed in plants from ore-bearing to barren areas. In
any event prospectors attempting to use the biogeo-
chemical method should be aware of these factors and
should have a rough idea of their possible influence on
survey results. Unfortunately the subject is complicated
and the data for many metals of interest to prospectors
is meager. Nevertheless some suggestions might be ob-
tained as to the approximate size of the variation in
plant metal content that is needed to justify additional
expenditures for detailed exploration.

It will be obvious in the following that the authors,
who are geologists, are heavily indebted to agricultural-
ists and plant physiologists as well as biogeochemists for
the data summarized.

Factors Related to the Plant

Kind of Plant. Warren and Delavault have con-
cluded, after considering the results obtained from hun-
dreds of plant analyses, that practically all trees and

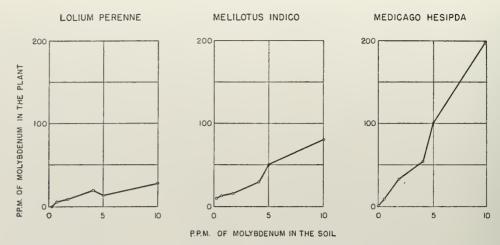| LOLIUM PERENNE | MELILOTUS INDICO | MEDICAGO HESIPDA |

P.P.M. OF MOLYBDENUM IN THE SOIL

FIGURE 2.   Graphs showing how different types of plants, growing under the same conditions, will take up different amounts of molybdenum from the soil. *Data from Barshad (1951).*

smaller plants are capable of reflecting mineralization. Any number of plant types can be used in sampling a given area but each will give a different biogeochemical anomaly which may vary considerably. While the pattern of the anomaly will generally be preserved, there is a chance that an anomaly could be overlooked if the plant type sampled absorbs only minor amounts of a given metal. The relative absorption of molybdenum by three different plant types serves to illustrate this problem. If at the beginning of a prospecting program one chose to sample *Melilotus indica* and during the course of a traverse changed to *Medicago hespida* the molybdenum content would increase by as much as 125 parts per million. This increase could be interpreted to mean the existence of an underlying ore-body whereas the metal content of the soil actually had remained constant. If on the other hand *Lolium perenne* were sampled at the same point a drop of 40 parts per million would be expected, and one might conclude that a mineralized area lay behind. Yet the plant type would be the only factor responsible for the variation.

Table 1.   *Nutrient Requirements of Different Plants.*

Plant	Element (%)		
	Ca	K	Mg
Sunflower	2.18	5.01	.640
Beans	2.11	4.02	.594
Wheat	.79	6.73	.406
Barley	1.87	6.92	.540
Peas	1.55	5.25	.504
Corn	.51	3.87	.402

After Newton (1928)

An even more striking example is the accumulation of selenium by certain species of *Astragalus*. In one investigation (Trelease, 1945), the average content of these accumulators was about 800 ppm, some plants containing as much as 15,000 ppm (1½ percent), many times the amount that would be lethal to ordinary plants. Wheat from the same soil averaged less than 5 ppm of selenium.

Large differences may exist between families, species, or varieties in their ability to absorb a given element under a given set of conditions. Many plants require abnormal amounts of molybdenum; horsetails absorb silica; and members of the family *Lycopodioceac* accumu-

late aluminum. Even the normal uptake of major ents varies within wide limits among plants of di groups. Table 1, modified from Newton (1928) illus the varying requirements of calcium, potassium magnesium by six common plants. All six plants grown in nutrient solution for 56 days, with five individuals of each type in the same crock. On green portion of each plant was analyzed.

The data of Collander (1941) showing variati uptake between plants are even more striking. The mum uptake for Na and Mn is about 20 to 60 greater than the minimum; for Li, Mg, Ca, an about 3 to 5 times the minimum; for K, Rb, an about 2 to 3 times the minimum. A given plan found to be consistently rich or poor in a given el regardless of the year of cultivation or the compo of the culture solution. An interesting relationship by Collander and also by Hurd-Karrer (1939) great similarity in the uptake by a given plant c ments that are chemically alike. Rubidium and c were found to be absorbed almost as rapidly as sium; strontium almost as rapidly as calcium; sele as fast as sulfur, and arsenic as fast as phosph Some plants appear to be able to screen out or to themselves against excessive uptake of some elem Plants do not contain silicon and aluminum, for ple, in proportion to their abundance in the soil. M algae generally contain abundant potassium and little sodium, although the concentration of these ments in sea water is in the reverse ratio. Pea roots found to absorb 2 to 3 times as much calcium Na-Ca bentonite as did barley roots, while at the time barley roots absorbed 4 to 5 times as muc dium as did pea roots (Elgabaly and Wiklander, 1 This is an effect that varies markedly between types, is different for different groups of elements soil materials and is likely to become known only extensive experimental work. Unfortunately almost ing is known about selective uptake of the micronutri or of metals present in minor amounts. In the ca sodium and calcium just described the disproportic uptake is reduced when the concentration of sodium calcium outside the plant is increased.

le roots of rice were found to protect themselves
: further absorption of copper ions after they had
-bed a certain amount (Isizuka, 1940). In another
Melandrium silvestre plants that had already grown
pper-rich soils were found to grow better than
s under experimental conditions of high copper
ly and in still another case large increases in the
nt of zinc in the soil did not result in proportionate
ases in the zinc content of the oat plant.

e are not aware of any cases, however, where selec-
uptake or shielding by healthy plants has been
n to result in a reverse relationship between metal
nt of a plant and metal content of the soil in which
lant is growing, all other conditions remaining
ant, although there are cases where the variation
ant metal content is negligible.

e experience of biogeochemical prospectors indicates
trees in general are more consistent in reflecting
netal concentration of the soil than are smaller
s. But the lesser plants in many instances show a
er contrast in metal concentration than do the trees
ing in a given area. The giant ragweed *Ambrosia*
a sampled by Harbaugh (1950, pp. 564-565) in the
tate district showed a variation in zinc content
5000 ppm to 1500 ppm between the mineralized
and the barren area. Among the trees the black
y (*Prunus serotina*) showed the largest variation;
iged from 2200 ppm zinc in the mineralized area to
ppm zinc in the barren area. Webb and Millman
l, p. 495) noted in their biogeochemical studies in
a, that there was little variation in metal content
en species. They showed that the background
s were especially constant among different plants
buted over wide areas.

nt Organ Sampled. After the absorption of soil
rials by the roots, each element travels to specific
of the plant structure. The translocation, or route
destination, of these nutrients is important in choos-
vhich organ to sample. In general, the newly ab-
d materials travel to the younger parts of the
. Therefore, these parts contain the highest concen-
on of metal and are the most satisfactory to sample.
ever, Warren and Delavault (1949, p. 541) working
copper and zinc in British Columbia, found that
aves, cones, and needles of trees gave inconsistent
ts. They recommend the use of twigs which were
1 to 3 years old and an eighth to a quarter of an
in diameter. The data summarized in table 2 are
on nine biogeochemical investigations which in-
d 75 tree samples, 13 samples of smaller plants, and
iety of metals. The organs are arranged in order of
asing metal concentration. In the tree samples the
s showed the highest concentration of metal in 49
nt of the analyses, and the twigs were highest in
ercent of the samples. The leaves contained the
st concentration in 77 percent of the smaller plants.

toradiographs taken by Biddulph and reported by
g (1951, pp. 261-275) substantiate the results tabu-
above. Biddulph introduced radioactive phosphorus
a nutrient solution which contained young bean
s; half of these were sampled after a period of four
and the others were transferred to fresh nutrient

Table 2. Organs with the highest metal concentration (in order of decreasing concentration).

Trees	Smaller plants
1. Leaves	1. Leaves
2. Twigs	2. Roots
3. Cones	3. Stems
4. Wood	
5. Roots	
6. Bark	

solution which contained no phosphorus. The plants
sampled after the first four days showed that the phos-
phorus had moved directly through the roots to the
younger portion of the plants. The remaining plants
were sampled after an additional four days and auto-
radiographs were made of them. The second set of
graphs showed that a considerable amount of the phos-
phorus deposited in the younger organs, at the time of
transplanting, had moved to the new plant organs devel-
oped during the second four-day period. Thus, not only
is there a continuous influx of material from the roots to
the younger organs but there is also a constant redistri-
bution of material to the younger leaves and twigs.

Age of Plant and of Plant Organ. After a plant
reaches a certain minimum age, which is different for
each plant type, the uptake of material from the soil—all
other things being equal—becomes constant and the re-
quirements of new growth cause only gradual increases.
While the plant as a whole may show no sharp variation
in nutrient content, the individual organs developed
during different growing seasons exhibit marked varia-
tions. Table 3, from Barshad's work with molybdenum,
contrasts the metal content of new tree leaves with those
of the previous year's growth. Tree organs from 1 to 3
years old give consistent results in addition to con-
taining the maximum concentration of metal. Younger
organs fluctuate in metal content while the oldest wood
consistently shows low concentrations.

The smaller plants reach a similar optimum at the
time of flowering when the metal concentration is at a
peak and the leaf functions are fully developed (Lun-
degarth, 1951). For these reasons the whole of a trav-
erse or area should be sampled at about the same time.

The combined effect of sunlight, rainfall, air tempera-
ture, as well as the plant itself is responsible for the
seasonal variation of metal uptake by plants. Robinson
(1943, p. 6) has checked the same trees for rare earths
on three different occasions. It was found on June 1
that the trees contained 174 ppm rare earths, on July 4
the total ppm had risen to 634, and by October 1, to
981 ppm. The same worker reported boron in samples of
hickory leaves doubled between spring and fall (Robin-
son et al., 1942). Barshad shows molybdenum in certain
plants varies three-fold from spring to fall. Warren et
al. (1947, p. 806) have noticed the seasonal variation
of copper and zinc in tree leaves.

Health of the Plant. If plant roots are injured
through toxic soil conditions or in other ways they may
lose their ability to absorb elements selectively or they
may absorb excessive quantities of some elements. A
single plant thus injured might yield an execessively
high assay which would not be duplicated in neighboring
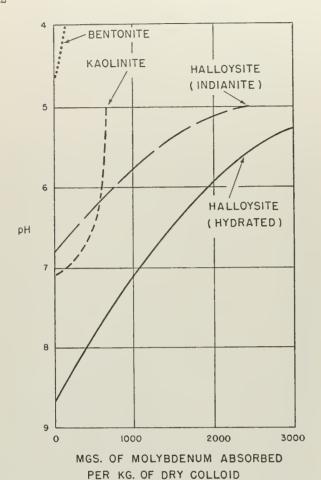plants and should therefore be rejected. But if all the

FIGURE 3. Graph showing amount of molybdenum absorbed by four types of clay minerals at different pH. *Modified from Barshad (1951).*

Table 3. Molybdenum content of new and old tree leaves.

Plant	Molybdenum in leaves (mgm./kgm.)	
	Current growth	Previous year's growth
Lemon tree_____	1.3	2.3
Mesquite_____	1.2	3.6

Modified after Barshad (1951)

plants within one segment of the area under survey are injured in the same way, this segment would yield high assays and unless the condition of the plants was recognized from some fairly obvious abnormality the anomalous segment might be treated as a valid suggestion of mineralization. Biogeochemical anomalies that correspond with marked differences in the physical character of the soil should be suspect.

Root Depth. The maximum depth at which a biogeochemical anomaly can be detected at the surface is determined principally by two factors: the depth to which the plant roots extend downward and the ion-dispersing forces working from the ore body upward.

The root systems of most plants extend into the soil only a few inches or feet at the most. While some root systems extend to depths of 80 feet and more, in gen[eral], deep roots are exceptional. Weaver (1919) limits [the] root depth of herbs and shrubs growing on the f[orest] floor to the upper 18 inches. Kelley (1923, p. 15) rep[orts] that the absorbing system of most woodland plan[ts is] concentrated within the soil's upper 12 cm and [a] depth of 30-70 cm. Further, he questions the gen[eral] assumption that trees have deeply penetrating tap r[oots].

The root depth appears to be less important in s[eek]-ing out high metal concentrations in the soil than [are] the forces that raise the ions from depth. Many bio[geo]-chemical studies have utilized both trees and le[sser] plants in a single investigation (Warren and Howat[t], 1947). There was no evidence to suggest that trees [were] able to tap high metal concentration at depths [not] reached by shallow-rooted plants.
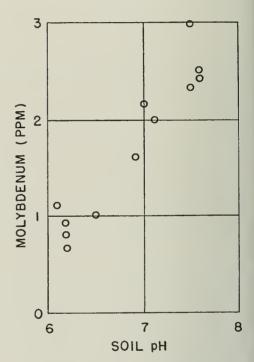
FIGURE 4. Graph showing amount of molybdenum taken up by alfalfa at different pH. Assimilation increases with decreasing soil acidity. *Data from Evans, Purvis, and Bear (1951).*

Chemical and Physical State of the Metal

Metals in the Soil Solution and in Mineral Gr[ains]. The soil is the principal source of the macronutrie[nts] water, phosphorus, sulfur, potassium, calcium, ma[gne]-sium and iron; the micronutrients, copper, zinc, mo[lyb]-denum, manganese, boron, and possibly silicon, col[?] and others, as well as the many metals not yet sh[own] to be of nutrient value to plants.

Metals may simply be dissolved in soil water and s[o] readily available to plants. There is also abundant [evi]-dence that plants can take metals directly from s[oil] minerals. A slowly soluble form of copper, for insta[nce] is commonly adequate for plant growth (Jamison, 19[?]). The form in which zinc is available—as zinc carbon[ate] freshly applied zinc sulfate, zinc applied in plant [?]

FIGURE 5. "Range of contents of some trace elements commonly found in mineral soils. Thin lines indicate more unusual values; certain extremely high contents reported from abnormal localities influenced, for instance, by ore deposits have been ignored." *From R. L. Mitchell, in Chemistry of the Soil, F. E. Bear, Editor, 1955. Courtesy Reinhold Publishing Corporation.*

al, or zinc accumulated in the soil from applications ne sulfate over 5 years—makes very little difference ts utilization by a plant (Shaw, Menzel and Dean, t). Plants are able to obtain phosphorus directly n relatively insoluble soil- or rock-phosphate, al-gh the ability to do so varies greatly from plant lant. Manganese may be available from very fine-ned manganese oxides (Jones and Leeper, 1951).

etals Held in the Soil by Ion Exchange. In typical of temperate regions, only a small fraction of the l metal content available to plants is present as dis-ed ions in the soil water or as a major component of eral grains. The larger part is sorbed [1] as cations or nions on various colloidal particles, principally clay erals and organic matter; it is bound to them with ls of varying strength and is therefore differentially lable to plants. Were it not sorbed in this way, most he mineral matter added to soils as soluble salts—n fertilizers, for example—would be leached rapidly n the soil and serve very little purpose. Or some me-c ions, only traces of which are required by the plant, ht be available in excessive, perhaps toxic, amounts. ome of the ions sorbed on colloidal materials are so tly bound that they are said to be fixed, and are ctically unavailable to plants under normal condi-s. Others can be released to the soil solution, or to its directly, or perhaps to other soil colloids, by the stitution of suitable ions. As an example, all or nearly he potassium sorbed on a clay might be replaced by rogen and carried away in solution if the clay were

ludes any process by which ions are held.

leached with an acid. And subsequently the hydrogen might be replaced by potassium or by some other ion or ions through leaching again with a solution containing these ions.

This process whereby cations or anions are exchanged between liquids and solids, or between solid and solid, is ion exchange. It affects both organic and inorganic components, and influences both physical and chemical properties of the soil. An essential step in assimilation of mineral elements by plants is the direct exchange of hydrogen ions released by the plant for mineral ions in the soil. Apparently this can take place with or without intermediate solution of the ions. The ion-exchange proc-ess is like other ordinary chemical processes in many ways, being reversible, stoichiometric (retaining elec-trical balance) and dependent upon the concentrations of the exchanged ions. The rate of reaction ranges from instantaneous to several hours, depending mainly upon the exchange material on which the ions are sorbed. The predominant exchange materials in soils are clay and organic matter, though other very fine-grained sub-stances possess exchange properties as well. Calcium carbonate, for example, is a very effective absorbing material in calcareous soils.

The cation exchange properties of clays are due to (1) Unsatisfied chemical bonds of clay crystal fragments balanced charges that can sorb cations (important in kaolinite and halloysite; less important in illite and chorite; and of minor importance in montmorillonite and vermiculite); (2) Unbalanced charges due to substi-tution within the lattice structure that may likewise be satisfied by sorbed cations (particularly in montmoril-

lonite and vermiculite); and (3) Cation replacement of the hydrogen in exposed hydroxyl ions (important in kaolinite and halloysite). Partly because there are these several causes of cation exchange and partly because the position of exchangeable cations relative to the clay mineral surface varies greatly, cations even of a given element are held with varying tenacity on a given clay mineral. Generally they are held with decreasing tenacity as the clay mineral becomes saturated with exchanged cations. Usually ions held as a result of broken bonds are around the edges of the clay crystals and are much more easily displaced than those held as a result of substitutions within the lattice structure. The relative energies with which cations of different elements are held, or the relative difficulty of displacing them, is not easily predicted. An order or replaceability $Cu > Pb > Ni > Co > Zn > Ba > Ca$ has been suggested (Mitchell, 1955 p. 265); but in view of the several causes of ion exchange, probably no one order of replaceability applies for all exchange materials. Generally, but not universally, the difficulty of displacing a cation appears to increase with valence and with size of the ion, and tends to decrease with hydration of the ion. Reducing the size of the clay particles, as in grinding, tends to increase the capacity of the clay to exchange cations—especially clays in which the main cause of cation exchange is broken bonds.

The cation-exchange capacities of clay minerals, measured in milligram equivalents (m.e.) of cation held per hundred grams of exchange material at pH 7, ranges from 3 to 15 for kaolinite, from 5 to 50 for halloysite, from 80 to 150 for montmorillonite and vermiculite, and from 10 to 40 for illite, chlorite, and attapulgite groups (Grim, 1953, p. 129). Natural soils are reported with a cation-exchange capacity of 200 m.e. or more per 100 grams of soil. Peaty soils are reported to have the highest capacities. Inorganic soils rarely have exchange capacities exceeding 75 m.e., and the great majority have less than 50 m.e. per 100 grams of soil. A soil with an exchange capacity of 50 m.e. per 100 grams could absorb over 15,000 ppm of zinc. Other ions, if also present, would, of course, compete with the zinc for exchange positions. Exchange capacity increases with pH; that is, exchange capacity is higher under alkaline conditions. Generally the number of ions held tends to vary with its concentration outside the exchange material.

In addition to, or instead of being absorbed as cations, some metals such as boron, molybdenum, selenium, and vanadium can appear as complex anions which are soluble in water and can be absorbed as anions by anion-exchange materials. Others such as zinc, copper, ferric iron, and thorium may form basic salts with clay as well as being absorbed as cations (Mitchell, 1955, p. 264). And in general, the higher the percentage of saturation by a given cation, the more easily that cation can be displaced and absorbed by plants (Jenny and Ayers, 1939). Thus, in a kaolinitic soil with an exchange capacity of 8 m.e. per 100 g, of which 0.08 m.e. (1 percent) was copper, the amount of copper available to plants should be greater than in a montmorillonitic soil with a cation-exchange capacity of 40 m.e. per 100 g, of which 0.2 m.e. (0.5 percent) was copper. In general, the heavy metals are less readily available to plants from montmorillontic clays than from kaolinitic clays. The

situation is complex where several ions compete fo[r] ex[...] change positions, the degree of saturation having [...]la[...] tively little effect on availability where the other s[...]ed[...] ions are held very tightly but having a very large [...]ect[...] on availability where the other ions are held loose[...] A[...] common result of this is that the availability of a l[...]vy[...] metal decreases as the ratio of sorbed sodium to s[...]ed[...] calcium increases.

Metals Held in the Soil Other Than by Ion Exch[...] ge[...] Through a process called "chelation" some metal[s] [...] able to form stable complex ions with certain or[...]nic[...] substances produced in soils. The metal thus che[...]ed[...] does not enter into reactions of its own but is ca[...]ied[...] along with the complex ion. It may be either less [...]il[...] able or more available to plants than it was b[...]ore[...] chelation. Relatively insoluble compounds of co[...]er[...] zinc, iron, manganese, aluminum and calcium ca[...] be[...] converted to soluble forms through chelation. The[...] ns[...] appearance of zinc and manganese deficiency symp[...] ms[...] in plants under conditions favoring greater mic[...]or[...] ganic activity, or when organic matter especially [...]he[...] plant roots is added to the soil has been ascribed t[...]he[...] formation of organic chelating compounds which [...]d[...] the needed metals available (Mehlich and Drake, [...] p. 322). Iron versenate and ferric citrate are che[...]ed[...] forms of iron that provide an available source of [...]o[...] for plants. On the other hand, Crooke (1954) has s[...]wn[...] that nickel supplied as nickel versenate to oats in [...]d[...] culture did not increase the nickel content of the p[...]nts[...] over that of control plants whereas nickel supplie[...] in[...] the same amounts as the soluble ion from nickel su[...]ate[...] increased the nickel content in the plants more [...]an[...] 10 fold, producing toxic effects. Therefore, the nick[...] in[...] the nickel-toxic soil studied by Crooke he thought [...]as[...] the chelate form associated with the soil organic m[...]ter[...] and thus was readily available to plants.

Under some conditions metals present as soluble [...]ns[...] may form relatively insoluble precipitates with si[...]le[...] anions such as hydroxide, carbonate, phosphate or [...]li[...] cate. That zinc, manganese, copper and cobalt ar[...] de[...] creasingly available as the alkalinity increases [...]ay[...] result from this. Bivalent iron and manganese ca[...] be[...] made much less soluble through oxidation to oxid[...] or[...] hydrous oxides.

Fixation. The term fixation does not appear to [...] a precise meaning. It is used by some people to ind[...] te[...] merely retention of a metal in the soil in a form [...] resists leaching by meteoric water and by others to [...]i[...] cate greatly reduced availability to plants. Bec[...]se[...] metals can be held in the soil in so many ways ar[...] in[...] such varying degrees there is no sharp distinctio[...] be[...] tween those that are exchangeable or otherwise avai[...]le[...] and those that are not. If the energy of binding [...] particular cation to a clay mineral, for example, ex[...]eds[...] the cation exchange energy of a plant root, the c[...]on[...] is unavailable to the plant. But other cations of the [...]me[...] element sorbed in a different way may be avail[...]le[...] Some of the zinc ions sorbed in some magnesium [...]y[...] are thought to become incorporated within the cr[...]tal[...] lattice of the clay mineral and are not exchang[...]ble[...] (Elgabaly, 1950). The amount of nonexchangeable [...]nc[...] on kaolinite was found to increase with grinding o[...] the[...]

attice structure to destruction. Appreciable fixation
ptassium on montmorillonite occurs on drying and
action of the lattice.

Chemical Properties of the Soil

The chemical composition of the soil, more than any-
n else, determines the chemical and physical state
d ence the availability of metals to plants. It also
nces the amount of metal taken up by plants.
co-organisms may compete for some nutrient metals,
ny produce substances that make metals either more
ls soluble in soil water. Of the several chemical var-
l, the abundance of competitive or complementary
nd the pH of the soil can have marked effects on
etal content of plants.

A dity or alkalinity of a soil is probably the most
p tant single factor likely to produce misleading re-
lt in biogeochemical prospecting. It has some effect
e vigor of plants and determines the distribution of
plant types that are sensitive to a particular
n in pH. Most plants that have been studied by
lturists, however, tolerate a wide range of pH for
h if the necessary nutrients are available. Probably
as its greatest effect on plant growth though con-
g the chemical state and availability of nutrient
nces. It may completely immobilize a metal in the
y causing its precipitation as an insoluble com-
u l. For example, carbonates and phosphates of cal-
and magnesium and carbonates, oxides and hy-
es of iron, copper, manganese, and zinc tend to
under alkaline conditions. Soil pH affects the ion
nge properties of clays and other exchange ma-
is. In soils with pH varying in depth, the part of
ot system that absorbs nutrients is governed by
ariation.

T normal range of pH in soils is between 3 and 9,
h locally the pH may be beyond this range. Cer-
plants thrive on abnormally acid or alkaline soils,
e salt bush (*Atriplex*) and glasswort (*Silicornia*)
prefer strongly alkaline soils. In general, plants
st suited to neutral or slightly acid soils. The soil
not constant and tends to become more alkaline
depth. Kelley, working in Chester County, Pennsyl-
reports the soil increases in acidity to a depth of
ntimeters then decreases (1948, p. 53). More com-
data by Barshad is summarized in table 4 (1948,
).

le. *Examples of the relation of pH to depth in various soils.*
(After Barshad)

Depth range (inches)	pH range
0 to 80	7.3 to 7.5
0 to 60	7.3 to 9.1
0 to 36	7.6 to 8.1
0 to 48	7.5 to 6.8
0 to 60	7.3 to 8.1
0 to 36	8.4 to 9.7
0 to 48	7.9 to 9.3
0 to 72	7.9 to 9.4
0 to 30	6.4 to 6.7
0 to 56	5.6 to 5.5
0 to 43	5.6 to 5.2

Pl nts themselves acidify soils by exchanging hydro-
ns at the root surface for soil nutrients. Parent
ends to influence soil pH especially of residual
where rainfall is low. Carbonate rocks, for example,

tend to yield alkaline soils. But in areas of high rainfall
the increased vegetation, the resulting humus and the
leaching of more soluble alkaline components tends to
produce acid soils. The mineral belts in California are,
in general, in mountainous regions where the soils tend
to be acid. Weathering of sulfide ore deposits tends also
to acidify soils. Acidic surface waters are fairly com-
mon near ore deposits.

There is evidence to suggest that copper is fixed in
alkaline soils. Experiments of Peech reported by Jami-
son (1942, p. 296) show that only 17 percent of copper
added to soil remains available at pH 4.0 and only a
trace at pH 6.0. A similar test by the same worker
showed 40 percent recovery at pH 3.1 and 10 percent
at pH 5.0 (1942, p. 295). However, Jamison reports
somewhat different results, with a soil pH of 4.0 he re-
covered all of the copper and at pH of 6.0 only 33 per-
cent (1942, p. 296). In spite of the lack of agreement in
these data, it has been established that copper precipita-
tion begins at near neutral pH and is complete in the
alkaline range. Warren et al. (1952, p. 483), in field
prospecting for copper, noted a similar influence of pH
on the solubility of this metal.

The influence of pH on the solubility of zinc is much
the same as on copper. Zinc is concentrated in plants
growing in soils with a pH range of 3.5 to 7, with the
majority of the samples having a pH of 4 to 5 (Fulton,
1950, p. 667). Robinson et al. (1947, p. 577) report that
nut and fruit trees resist the absorption of zinc in alka-
line soils. The solubility of zinc in alkaline soils can be
materially increased by the addition of acid to the soil
(Aldrich and Turrell, 1951, p. 89).

Manganese, like the previous two metals, is absorbed
more readily by plants in an acid environment. Mulder
and Gerretsen (1952, p. 229) have shown that manga-
nese is highly soluble below pH 5.5 but with increasing
pH the metal is converted to the manganic oxides
(Mn^{+++} and Mn^{++++}) and as a result becomes less avail-
able to the plant. Brenchley et al. (1936, p. 182) have
observed a similar reaction where manganese is unavail-
able to plants in alkaline soils. The same conclusion was
reached by Fujimoto (1948, p. 132) working in Ha-
waiian soils and also by Aldrich and Turrell (1951, p.
89). Aluminum is reported to be available to plants in
two pH ranges: 4.5 and below, and 8.0 and above (Meh-
lich, 1942, p. 121). However, previous work showed
aluminum as the silicate is precipitated between pH
3 and 5 and also at pH 9 to 14 (Hartsock and Pierce,
1952).

Both tungsten and molybdenum are available in the
alkaline pH range. Tungsten and molybdenum are pre-
cipitated as ochers in a pH range of 3 to 5 (Hartsock
and Pierce, 1952; Clark, 1924). Molybdenum is ex-
tremely sensitive to slight pH changes in certain ranges.
Barshad has shown that a pH change of 0.8 in an acid
sandy loam resulted in a hundred percent increase of
available molybdenum, and a pH change of 2.7 in a
clay soil more than doubled the available molybdenum
(1948, p. 189).

Other metals such as barium and boron have been
studied by various workers. Roberts (1948, p. 74)
reports that he found no correlation between barium
content and pH. However, Mehlich (1942, pp. 121-122)
reports the absorption of barium in inorganic soils

reaches a maximum between pH 8 and 9; in organic soils between pH 6 and 8. Brenchley (1936, p. 175) states that boron is unavailable to plants in the alkaline range (1936, p. 175).

The accompanying table summarizes the effect of soil pH on the availability of certain elements to plants.

Table 5.   Effect of pH on the Availability of Elements to Plants

Elements more available in acid soils	Elements more available in alkaline soils
Aluminum *	Aluminum
Iron	Calcium
Manganese	Magnesium
Copper	Sodium
Zinc	Potassium
Boron	Molybdenum
Phosphorus †	Tungsten
	Selenium
	Silicon
	Barium

* Aluminum is available to plants in two pH ranges, (1) 8.0 and above, (2) 4.5 and below.
† Most available in mildly acid soils pH 6-7. Increasingly unavailable at pH < 5.0.

The uptake of a metal also can be influenced very strongly by other elements or radicals for reasons ranging from simple competition for exchange positions to very complex metabolic relationships that are not well understood.

For example, addition of phosphate in amounts likely to be used in ordinary fertilization practice has been found to cause the increase of the molybdenum content of crop plants as much as 10 fold. Addition of sulfate as gypsum decreased the molybdenum content of the plants as much as 6 fold (Stout, et al., 1951). Barshad (1951, II, p. 397) found the effect of phosphorous on molybdenum to be much more pronounced in acid than alkaline soils. Manganese sulfate inhibits the uptake of molybdenum by cauliflower and lettuce but not by spinach, tomato or white clover (Mulder, 1954).

The zinc content of oats decreased two- to four-fold with a 20-fold increase in the amount of calcium carbonate in the soil and decreased almost two-fold with a 15-fold increase in phosphate (Rogers and Chih-Hwa Wu, 1948). Zinc combining with phosphoric acid in the soil forms $ZnPO_4$ which is unavailable to plants (Robinson, et al., 1947, p. 597; Davis, 1941, p. 84). Increased soil nitrogen and potassium decreased the zinc content of orange leaves by as much as 5 percent (Reuther and Smith, 1950). Variations of two- or three-fold in the distribution of manganese in potato plants and in the manganese content were caused by altering the amounts of iron, potassium, phosphate, or calcium carbonate in the soil (Bolle Jones, 1955). Manganese tends to be available in the presence of sulfur, chlorides and iodides, but is fixed by fluorides and bromides (Fujimoto and Sherman, 1948). A significant increase in the uptake of nickel by oats was caused by an increase in the rate of supply of phosphorous but not by an increase in other major nutrients (Crooke and Inkson, 1955). Copper sulfate added to peaty soils decreased uptake of iron enough to cause chlorosis of corn plants (Willis and Piland, 1936). Similar interaction between iron and manganese, copper and nickel, copper and zinc, copper and molybdenum, copper and manganese, manganese and aluminum and calcium and manganese are also reported (Mehlich

and Drake, 1955). The presence of such ions as Ca^{++}, Ba^{++}, Al^{+++} and Fe^{+++} has been observed to stimulat uptake of K^+, Rb^+, Cs^+ and Br^- under some cond (Overstreet and Jacobson, 1952, p. 190).

Certain elements apparently are able to protect against the toxic effect of excess metals without red uptake of the toxic metal by the plant. Thus alum has been found to decrease the toxicity of excess c in citrus plants but does not inhibit the uptake of c by the plants. An increase in the rate of supply of : gen, potassium, calcium or magnesium decrease toxic nickel symptoms in oat plants but does not the uptake of nickel (Crooke and Inkson, 1955).

Physical Properties of the Soil

The soil structure is a controlling factor in the tion, drainage and temperature of the soil. The stru is partly dependent upon the size and shape of th particles; soils containing a high percentage of the fractions tend to be compact, to have poor drainag to contain relatively little soil air. Soil temperatu affected by the structure, water, and humus conten color of the soil as well as climatic factors. Since tion and temperature affect the rate of minera accumulation in plants and since drainage may affect the local supply of aerated water and metal these physical properties can be expected to infl the metal content of plants.

The size of soil particles, metal content and availability commonly are related. Soil samplin heavy metals (lead, copper, zinc) in northern Sask wan showed a close correlation between clay cc and amount of metal; clay soil containing up to 8 as much heavy metal as sandy soil over an unminer area (Byers, 1956). Roberts (1949, p. 73) has the particle size of the soil may correlate with its b content. Soil samples with an average size of 0.0 contained several percent more barium than th 1.65 mm. Barshad (1948, p. 189), working with denum, reports that particle size has little effect concentration of this metal in the soil. On the ba 27 samples Lovering and Huff (1950, p. 507) rep average copper concentration at San Manuel of 36 in the silt and clay fraction of the alluvium an ppm copper in the more coarse fraction. Rudrin pp. 19-25) has demonstrated that the fine fracti gray limestone soils contain more phosphorous tha coarse fraction. Since the clay fraction commonly mulates in certain layers or horizons in soils, size s is partly responsible for the uneven distributi trace elements in soil profiles. Without questio greater metal content of clay-sized material mainly from the greater ion exchange capacity in as well as the leaching of metals from more perm sandy soils.

Reitemeier (1946, p. 211) working in arid re has demonstrated the effect of increasing soil moistu solubilities of different ions. By increasing the mo in six different soils he found that calcium and n sium increased in four soils and continually dec in one. Chloride and nitrate decreased by 32 to 5 cent on dilution.

effect of soil moisture on pH is described by Hass
, p. 39); he found pH decreased as moisture de-
d.

Mitchell (1955, p. 271) has reported a remarkable
bization of Co, Ni, Fe, V, Cu, and Mn in soils that
ery poorly drained. Several times as much metal
extracted by 2.5 percent acetic acid or neutral nor-
ammonium acetate from poorly drained soil. Fuji-
and Sherman's work (1948, p. 144) with manganese
that this metal is released by a waterlogged soil,
by a damp soil and released by a dry soil. In-
solubility of molybdenum, silver and lead is
in other poorly drained profiles. The cause of this
bization is probably chemical though it is also known
repeated and intensive drying of clay soils increases
capacity to fix some metals.

Although the magnitude of the effect caused by varia-
in physical properties of the soil along a traverse is
known, biogeochemical anomalies that coincide with
ges in soil structure or with soil moisture content
as from dry ground to swampy ground should be
mined very critically.

Environment

Since photosynthesis controls salt accumulation, it is
likely that plants growing in the shade will ab-
different amounts of metals than plants growing in
un and in the same soil. The uptake of zinc by
was found to increase with temperature and dura-
of light (Ferres, 1951). Experiments with Cuban
co have shown that these plants accumulate more
al matter when shaded than when they are in the
sunlight.

The rate of transpiration or the volume of water ab-
d by healthy plants appears to have little effect
e amount of metal taken up though the rise of
in the stems may facilitate translocation of ions
indirectly affect uptake. Uptake of solutes may be
nearly proportional to absorption of water if the
roots are injured.

Lovering et al. (1950, p. 509) report that the amount
recipitation in humid and arid regions influences
accumulation of copper by plants. Roberts (1949,
) working with barium shows this metal is more
able to plants in areas of high rainfall than in areas
w rainfall. Low rainfall increases the iron and de-
es the manganese in plants (Warren et al., 1952b,
2).

The marked variation in metal content of plants from
n to season may be in part a result of chemical and
ical effects of climatic changes on the soil. The ex-
ageable copper in a soil was found to vary from week
ek, ranging from 46 grams per acre in late June to
grams per acre in mid-September, and back to 57
as per acre in November. The autumn rise was at-
ilted to greater moisture since the soil yielded less
er when dried before extraction. Sherman and
ner (1943), on the other hand, found more manga-
could be extracted from a soil if it were first
ed to dry. Roberts (1949, p. 67) reports no signifi-
correlation between temperature and the amount
arium in the soil. In areas of considerable relief,
ations in the weather that produce strong differences
il temperature and soil moisture content exist and

can be expected to affect plant metal content. This may
account for the observation of Warren et al. (1952, p.
437) that in many areas the metal content of plants on
north and south slopes differs markedly.

Plants showing deficiency symptoms for certain metals
sometimes can be ''fertilized'' by spraying leaves and
stems with solutions containing the metal needed. Iron,
copper, manganese and zinc are often supplied as sprays
and arsenic can be injected from insecticide sprays. It is
quite likely that small amounts of metal carried from
smelters or from ore dumps by the wind as fumes or as
dust could accumulate in plants in this way. This might
result in a misleading anomaly even though the plants
are thoroughly washed prior to ashing and analysis.

Summary

The exchange capacity and the energy with which
ions are bound will largely determine the amount of
metal taken and retained by the soil from soil solu-
tions or from solids. These may be major factors, then,
in establishing or preserving anomalously high metal
contents in soils over ore bodies. Not much is known
about the exchange relations between soil materials and
metals present in minor amounts. Field data mentioned
above suggest that variations of a few fold in metal
content of the soil can occur solely because the clay or
organic content of the soil changes markedly. Several
successful trials of soil sampling over known ore bodies
indicate that in these cases at least the excessive amount
of metal ions in soils over the ore was sufficient to
blanket effects due to variations in the soil alone. Never-
theless variations in soil metal content that coincide with
obvious changes in soil conditions, such as clay or or-
ganic content would need to be interpreted cautiously.

The metal content of a plant growing on these soils is
dependent upon the availability of the metals to the
plant. Because plants obtain the metals very largely
through the base exchange properties of their own roots
they must compete with other exchange materials and
absorbents in the soil and with other plants and micro-
organisms for these metals. Those exchange materials in
the soil that have a high binding energy for a given
cation also release that cation less readily to plant roots.
Quantitative data here are also very sparse. Chemical
extraction of metals from soil by leaching with dilute
acetic or hydrochloric acid, neutral normal ammonium
acetate, hot water and other solvents is commonly used
to get an indication of the availability of metals to
plants. The method is not entirely satisfactory. On the
basis of such extractions, for example, there is commonly
a large overlap in apparent availability between soils
that are deficient and soils that are adequate in some
nutrient metals.

The effect of the presence of other ions is too complex
and too variable between kinds of plants to permit much
generalization. Cases were mentioned above where the
presence of one metal caused the uptake of another to
change by as much as ten fold. The strange correlation
of the ratio of copper to zinc content of plants with
mineralization in cases where neither the copper nor the
zinc alone correlated reported by Warren et al. (1949)
and White (1950) is probably a manifestation of similar
metal relationships.

Because the main purpose of biogeochemical prospecting is to obtain a cheap and rapid indication of possible mineralized areas it is hardly practical to make an extensive soil survey for variations in the many complicating factors. In small areas the variations may be insignificant. Attention can be given to the physical condition of the soil and also to the bedrock. Limestone and dolomite are important in that they contain the carbonate ion. This ion may alter the pH of the soil or the carbonate radical itself may enter into chemical reaction with the metal sought. Riddell (1952), working in limestone terrain on the Gaspé Peninsula, reports zinc salts form soluble carbonate compounds, while copper and lead form insoluble compounds. The influence of a high percentage of carbonate may have been responsible for the apparent inactivity of copper and lead in the limestone terrain of the Tri-State district. Harbaugh (1950, p. 563) testing for zinc, copper, lead, tin, nickel, cobalt, and silver, reported only zinc showed any significant variation from place to place over the mineralized area.

The chemical effect produced by serpentine parent rocks has been discussed by Walker (1948, p. 475). In the three principal serpentine soils tested, molybdenum was deficient in that it was unavailable to plants. This relationship has been discussed under ion exchange above.

In areas where evaporates predominate care should be taken in evaluating biogeochemical results for certain metals. Riddell (1952, p. 184) suggests sulfates of zinc and copper are highly soluble while lead sulfate is insoluble in ground waters associated with these deposits. Barshad (1951, p. 387) has shown that sulfate decreases the solubility of molybdenum. Fujimoto (1948, p. 132), working with manganese, reports large amounts of chlorides release this metal in the soil. Sodium-salts tend to mobilize copper by a dispersive effect with the acetate more active than the chloride (Jamison, 1942, p. 297).

It is reasonably certain that the choice of plant and plant organ sampled will not materially affect the pattern of a biogeochemical anomaly provided that the variation in soil metal content is large and that the same organ and plant are sampled throughout the survey. The survey should be completed within a few days. It should be remembered also that biogeochemical prospecting is a cheap and rapid adjunct to other techniques. We doubt that a variation of only two or a few fold in the metal content of plants is sufficient in itself to justify expensive exploration. The anomaly should first be checked through sampling other kinds of plants, through sampling the soil or through use of other geological and geophysical techniques.

BIOGEOCHEMISTRY OF MOLYBDENUM

Molybdenum, which is not found in the native state, occurs in thirteen minerals, the most important of which is the sulfide, molybdenite. Molybdenite is genetically associated with late acid igneous rocks, in granites, pegmatites and aplites. It is known to be found in contact metamorphic deposits and in fissure veins, in both deep-seated and near-surface deposits. Molybdenum is associated with cassiterite, scheelite, wolframite and fluorite

Table 6. *Molybdenum in soils.*

Number of soils tested	Location	Range	Average	Reported by
20	California	0.1 — 9.7	2.01	Barshad
--	Wyoming	0.08—20.0	--	Stanfield
18	New Jersey	0.8 — 3.3	1.99	Evans and Purvis
79	Hawaii	7.9 —73.8	25.8	Fujimoto and Sherman
6	Hawaii	18.6 — 1.8	9.1	Edgington
20	Europe	4.3 —69.0	27.8	Bertrand
8	France	1.0 — 0.3	0.5	Edgington
--	Russia	-- — --	2.6	Vinogradov and Vinogr...
187	Argentina	-- —24.0	2.0	Trelles and Amato

Data from Robinson and Alexander (1953)

in vein deposits, and with lime silicates, scheelit... chalcopyrite in contact metamorphic deposits.

Molybdenum ranks 34 in relative abundance... the elements. Sea water contains but a fraction (... of a part per billion of this metal as do many... waters. The average molybdenum content of the... crust has been reported to be 10 ppm by Fersm... quoted in Wells (1937). However, Rankama and S... (1950) have recently placed the average for th... ment between 2.5-15 ppm while Mason (1952,... believes 15 ppm is nearer to the true average. In g... soils contain from one part per billion to a few... per million molybdenum. Robinson et al. (1951, p... report that average United States soils range fro... to 3.5 ppm molybdenum. The same authors show... the average molybdenum content of 500 soils fro... United States, South Africa, Alaska, Hawaii, ... Rico and Australia is 2.3 ppm (Robinson and Alex... 1953, p. 288). This result combined with the resu... 237 Argentinian and Russian soil analyses giv... average of 2.5 ppm molybdenum; Barshad (195... ported a soil range of 0.8 to 10 ppm. While the... denum concentration of some soils may reach man... of ppm in certain areas of the world (Hawaiia... contain as much as 73.8 ppm), the average for all s... probably below 10 ppm (Robinson and Alexander,... p. 288). The accompanying table shows the molyb... content of soils from eight widely separated area...

Kuroda and Sandell (1954) give the following... age concentrations of molybdenum in various... granitic rocks 1.1 ppm; basalts and diabases 1.1... gabbros 0.6 ppm; ultramafic rocks, including 9 se... tines, 0.5 ppm; organic-poor shales, 1 ppm; lime... and dolomites less than 0.5 ppm.

Plants and animals require molybdenum for n... life processes as this metal functions as a cataly... regulating the complex chemical reactions that... place in living cells. A deficiency of molybdenu... plants produces a variety of effects, the most comm... which is yellowing leaves and failure to produce fr... conditions that can be corrected by adding trace am... of molybdenum to the soil. Leaves of the lemon... were demonstrated to be normal when they cont... more than 0.24 ppm of molybdenum but those cor... ing 0.01 ppm were deficient; a lower limit of 0.01... below which plants exhibit malnutrition effects has... determined. The essential role that molybdenum... in plant nutrition has been demonstrated by... workers including Arnon and Stout (1939) and S...

1941). The effect of molybdenum in plant growth
shown in legumes in which it accelerates nitrogen
by bacteria. In Australia the application of
late to soils increased the yield and nitrogen con-
legumes, but nonlegumes showed no change
(Iffer and Linz, 1952, p. 112).

ough the necessity for molybdenum in plants has
stablished, there is much less agreement among
with respect to toxicity resulting from high con-
tions of this element. Killeffer and Linz (1952,
) stated that excessive amounts of molybdenum
jure plants. On the other hand Barshad (1948,
) believed molybdenum has no apparent toxic
Barshad's conclusion is supported, at least for
trations of less than 300 ppm, by the high molyb-
content of many plants: corn 46.8 ppm, alfalfa
pm, sunflower 15.9 ppm, tomato 34.0 ppm, and
pis 281.0 ppm, none of which exhibited toxic symp-
Stiles (1946, p. 134) reported the following molyb-
concentrations in different plants: clover 156
imothy 30 ppm, rye grass 54 ppm, and Yorkshire
8 ppm.

minor amounts of molybdenum are required for
hy plant; but many plants concentrate this metal
h as a thousand fold from the soil in which they
(Killeffer and Linz, 1952, p. 112). Lewis, as re-
te by Stiles (1946, p. 134), showed clover, a member
legume family, assimilated more molybdenum than
oier plants by ratios of as much as seventeen to one
an average of by five to one.

ashad, working with 22 plants in soil of pH 8, has
dstrated that there is a difference between total
lenum content of the soil and the fraction that
ilable to the plant (average ratio 2:1). Further,
ows the accumulative powers of those plants in
great quantities of molybdenum when the soil
is but minor amounts.

*Average molybdenum content of plants as related to
molybdenum content of soils.*

PLANT[2]	Concentration*					
Mo	10	5	4	1.5	0.5	trace
ble[1] Mo	6	3	2	0.8	trace	trace
americana	220	--	--	--	--	--
hespida	200	100	54	36	8	0.8
niculatus	150	40	47	16	11	4
repens	150	80	50	12	5	3
fragiferum	--	--	50	12	5	4
subterraneum	175	50	--	--	--	--
alba	80	30	77	18	22	5
officinalis	80	28	55	14	5	2
indica	80	50	30	15	13	7
sativa	30	15	16	13	5	1.3
vulgare	27	--	--	--	--	--
tiva	21	5	7	6	4	2
vulgare	18	17	--	--	--	--
yana	40	14	13	5	--	--
erenne	33	10	18	7	4	2
atior	--	--	7	2	--	--
glomerata	--	--	9	5	--	--
dilatatum	9	2	4	2	--	--
vulgare	7	2	--	--	--	--
dactylon	11	3	7	4	--	--
halepense	5	--	--	--	--	--
cicutarium	--	--	13	2	--	--

Modified after Barshad (1951)

pp dry matter; first one foot of soil.
ou of total soluble at pH 8.
cate; stems and leaves.

Background values have to be determined in barren
areas for each biogeochemical study. However, certain
tentative limits have been established for molybdenum
in plants by Barshad and by Robinson. Barshad's values
range from a trace to 220 ppm; Robinson gives a range
of a trace to 137 ppm. In general the average will be
below 100 ppm and in most cases above 10 ppm.

As a general rule, analyses of most plants growing in
soils containing high concentrations of molybdenum will
show a biogeochemical anomaly. However, the lesser
plants, especially the legume family, reflect the soil con-
centration most effectively. The following plants are well
suited to biogeochemical prospecting and have been used
successfully in molybdenum studies:

Table 8. Plants useful in prospecting for molybdenum.

Coreothrogyne filaginifolia (Wooly aster)
Devils paint brush
Vicia americana
Medicago hespida
Lotus corniculatus
Trifolium repens
Trifolium fragiferum
Trifolium subterraneum
Melilotus alba
Melilotus indica
Melilotus sativa
Triticum vulgare
Avena saliva
Horedum vulgare
Chloris gayana
Lolium perenne
Cneoridium dumosum
Quercus weslenzenii (Interior live oak)
Quercus douglasii (Blue oak)

Misleading Anomalies

Exchange Material pH, and Other Ions. As the pH
and exchange material in the soil are closely related,
they have a combined effect on the availability of molyb-
denum to plants.

Clay is the most common and effective exchange mate-
rial in the soil. It is possible that clays, through differ-
ential absorption, may nullify the effect of a large
concentration of molybdenum in the soil. The amount of
absorption depends primarily on the soil pH and sec-
ondarily on the type of clay. Organic exchange materials
become important only when the organic content of the
soil is abnormally high. An accompanying figure, taken
from Barshad's studies with molybdenum, illustrates the
relationship between pH, clay type and availability of
molybdenum to plants.

The pH controls molybdenum availability through its
effect on solubility and through its effect on absorption
of molybdenum by clay minerals.

The solubility of molybdenum minerals increases di-
rectly with decrease in pH of the soil solutions. As the
molybdenum minerals near an ore deposit have not
completely lost their identity, much of the soil molyb-
denum will be in the mineral form. The acid conditions
common near ore deposits may, however, promote the
decomposition of the mineral compounds to release
the molybdenum. An accompanying table illustrates the
solubility of molybdenum minerals in water, sodium
hydroxide and hydrochloric acid.

Once freed from the other elements in the mineral
compound, molybdenum forms complex ions with oxy-
gen, the most common of which is the divalent oxide

Table 9. *Solubility of molybdenum minerals in various reagents.*
(Mo in ppm)

Reagent	Molybdenite MoS₂	Ferrimolybdite Fe₂(MoO₄)₃·7.5H₂O	Wulfenite PbMoO₄	Molybdic oxide MoO₃
H₂O	0.05	5.4	0.014	250
0.1N Na(OH)	0.44	88.0	27.4	Very sol.
0.1N HCl	2.84	168.0	3.0	130

After Barshad (1951)

MoO₄⁼. It is at this point in the chemical history of molybdenum ions that they are likely to be absorbed by the clay fraction of the soil. Barshad (1951, p. 299) stated that soil molybdenum is in three forms: (1) as a soluble molybdenum salt, (2) as a component of soil organic matter, and (3) as the absorbed exchange anion MoO₄⁼. The newly formed complex ion is of such size that it can enter into exchange relationships with the OH radical in the clay fraction of the soil. There is a potential set up between the OH ions in the clays and the molybdenum complex which favors exchange and is governed by the pH. To illustrate this, Barshad (1951, p. 298) has shown that a removal of molybdenum from acid clays results in an increase in pH. The greater the pH, the smaller the amount of molybdenum absorbed into the crystal lattice of the clay until at pH 7.5 virtually no molybdenum is absorbed (Barshad, 1951, p. 298). Therefore, only in alkaline soils does this ion become available to plants in any significant amount.

Table 10. *Relationship of molybdenum in plants to soil pH.*

Plant	pH range	Increase of Mo in plant (ppm)
Ladino clover	5 to 7	10
Ladino clover	5.3 to 7	66
Ladino clover	6 to 7	58
Ladino clover	5.3 to 7	39
Ladino clover	5.3 to 7.5	26
Lotus corniculatus	5.7 to 7.5	96
Lotus corniculatus	5.3 to 7.5	74
Rhodes grass	7.3 to 7.9	15
Rye grass	7.1 to 8.5	—3

After Barshad (1951)

The work of Evans, Purvis and Bear (1951, p. 118) on alfalfa in New Jersey's Nixon loam demonstrated that the molybdenum concentration in alfalfa increased with higher pH. Their results are shown in an accompanying figure, and show clearly the changes in concentration with increase in pH.

When the pH exceeds 7.5, molybdenum is again absorbed but in smaller amounts. An accompanying table shows the reabsorption of molybdenum in the alkaline range as well as the general increase of alkalinity with depth shown by most mature soils. The concentration of molybdenum at the surface could also be attributed to enrichment by many cycles of plant growth which absorbed molybdenum and subsequently contributed it to the surface soil layer after death.

Walker (1948, p. 475), working with the serpentine soils of northern California, has shown these soils to be abnormally low in available molybdenum. He believed this to be a general condition of all primary soils derived from serpentine parent material. He thought it to result partly from the inherently low molybdenum content of

Table 11. *Relation of available molybdenum to pH at d...*

Soil type	Depth (inches)	pH	Available molybdenum (i...
Sandy loam	0-12	7.3	3.3
	12-24	7.9	2.6
	24-36	7.4	2.1
	48-60	8.1	1.8
Clay loam	0-12	7.3	6.8
	36-48	8.7	5.8
	48-60	9.1	3.0
Clay loam	0-12	7.5	2.9
	12-24	7.2	2.5
	36-48	6.8	1.3

Modified after Barshad (...

serpentines; it may also result partly from the fi...... of molybdenum in clay molecules. Clays derived ...... serpentine rocks are high in magnesium, a metal ...... chemical activity and ionic radius are similar to n...... denum.

Table 12. *Some ions that affect the uptake of*
molybdenum by plants.

Ions that stimulate the uptake of Mo	Ions that suppress the uptake of Mo
PO₄	CO₃
Cl	HCO₃
NO₃	OH
	SO₄
	S
	N
	FeO

Compiled from several sources.

Changes in the chemical makeup of soil are di...... to recognize in the field. Only under optimum cond...... is it possible to correct errors that are the result...... lack of knowledge of the exact soil chemistry. O...... the most common sources of change in the ionic con...... tion of the soil is due to a change in underlying ...... type, and the investigator who crosses a contact bet...... two rock types without recognizing it may recor...... anomaly where none exists. There are many rocks ...... could introduce sufficient foreign ions to produce ...... a misleading anomalous effect; some of these are ...... in an accompanying table.

Table 13. *Sources of detrimental ions.*

Rock type	Ion supplied to the ...
Limestone and dolomite	CO₃, HCO₃
Playa deposits (salines)	SO₄, Cl, OH, N...
Basalt	PO₄
Gossan	S, SO₄

Season. Plants, as the result of cyclic chang...... their physiology, contain different amounts of mi...... material during different times of the year. The ...... change in the assimilation of molybdenum by plant...... been studied by Barshad; his results are summariz...... the accompanying table. This cyclic change with re...... to molybdenum as reported in the lesser plants i...... reflected in deciduous trees.

Age of the Plant and Organ. As the plant deve...... certain chemical and physical changes take place ...... alter the amount and kind of material that the ...... will require from the soil. Similar changes are rep...... in the development of each organ.

ae 14. Effect of season on molybdenum content of plants.

Plant	Location*	Molybdenum in leaves		
		Spring[1]	Summer[2]	Fall[3]
.lfa_____	Coloma_____	16.0	20.0	28.4
.lfa_____	Buttonwillow____	9.2	11.3	18.0
ilos alba_____	Pond_____	--	32.0	77.5
ilos alba_____	Greenfields_____	18.1	44.8	--
is rniculatus_____	Greenfields_____	30.0	43.6	92.9
is rniculatus_____	Wasco_____	20.6	31.0	72.0
de rass_____	Buttonwillow____	8.1	14.0	25.0
g s_____	Greenfields_____	2.5	4.3	6.5
g s_____	Shafter_____	4.3	7.5	10.0
na grass_____	Pond_____	1.7	5.0	--
na grass_____	Shafter_____	3.6	4.9	9.8
er ass_____	Buttonwillow____	3.9	--	8.2
an u grass_____	Greenfields_____	4.0	--	7.6

After Barshad (1951)

[1] Kern County, California.
[2] ril ay.
[3] ne ly.
[4] pte er-October.

[t s necessary, therefore, to sample growth of the
ne age. Second year stems and leaves have proven
b the most satisfactory.

T nslocation. After absorption by the root system,
utrient materials are transported to different parts
t plant structure. Molybdenum, as evidenced by
t diographs, moves directly into the interveinal
i s of new leaves in most plants (Stout and Meagher,
8 p. 473). In legumes, accumulation is centered at
ed pods (Killeffer and Linz, 1952, p. 112). Stout
d Meagher (1948, p. 437) state that molybdenum is
t sorbed in the stems of plants to any large degree,
t arshad found, after testing 14 plant types and 34
a s, the highest molybdenum concentration was found
b in the leaves of 16 of the plants, in the stems of
a d in the roots of four.

Field Studies

T ee areas in California were studied to determine
w iogeochemical prospecting can be used to indicate
n mally high concentrations of molybdenum in the
l. Factors (reported in the agricultural literature)
at nfluence the concentration of molybdenum in soils
d lants were observed in the field and their impor-
g to biogeochemical prospecting evaluated. Molyb-
n n, in the minerals molybdenite or powellite, was
o n to be present in all areas. In all but one area
e etal was concentrated in definite zones. The plant
v e soil, geology, climate, and topography differ
a y in the three areas.

S ecimens of several species of trees and smaller
a s were collected. At certain stations old and new
h was collected for comparison, as were different
r s of the same plant. In each area soil samples
r taken where feasible and the pH determined. The
r ipal clay in the soil at the Bour molybdenum mine
s identified by X-ray methods and its concentration
c lated. Molybdenum concentration in the soil in
s rea was also determined.

T o methods of plant analysis were used in these
i es. Quantitative spectrographic methods were used
alyze samples collected at the Bour molybdenum

*Table 15. Variation of molybdenum content of plant
leaves of various species.*

Plant	Milligrams of Mo per kilogram of dry matter
Desert athel (tamarisk) _____	34.0
Black locust _____	15.9
Eucalyptus _____	1.4
Cottonwood _____	1.6
Yellow sweet clover _____	59.3
Cowpeas _____	141.0
Alfalfa _____	20.7
Perennial rye grass _____	11.6
Tall fescue _____	14.9
Prairie brown grass _____	8.7
Wheat stubble _____	26.4
Sweet corn _____	46.8
Mullet _____	50.4
Sunflower _____	15.9
Watermelon _____	14.1
Cantaloupe _____	1.3
Tomato _____	34.0
Malvarotundifolia _____	66.0
Cotton _____	21.6
Romie _____	11.8

After Barshad (1951)
All grown in Merced clay loam, Buttonwillow area, Kern County, California. Surface
foot contained 6 mgm of Mo/Kgm. pH 7.2.

mine, whereas a wet chemical technique, developed by
the U. S. Geological Survey, was used to analyze the
samples from the other two areas.

Areas for study were chosen where diverse soil, plant,
and climatic conditions could be expected. These areas
demonstrate, to a limited degree, the variation in results
that can be expected when prospecting for molybdenum
using biogeochemical techniques.

Bour Molybdenum Mine

At the Bour molybdenum mine, 6 miles west of Ra-
mona, San Diego County, California, molybdenite is
disseminated as flakes in a northwest-trending aplite
dike that cuts the Cretaceous Woodson Mountain gran-
odiorite. The ore is reported to average 0.5 to 1.0 percent
molybdenite. The dike ranges from 30 to 300 feet in
width. A 240-foot adit driven from the northeast inter-
sects the dike 200 feet below the surface. Two open cuts
are south of the adit.

Two biogeochemical traverses were made across the
dike; one 260 feet long, bearing N. 68° E., was 300 feet
south of the adit; the other, 135 feet long, bearing N.
80° E., was 700 feet south of the adit and entirely
within the dike. The samples were collected in Febru-
ary 1954.

Biochemistry. Leaves and stems of *Cneoridium
dumosum* were collected at each station. This plant,
which is widely distributed throughout the region, is
more abundant on the granodiorite, where a deeper soil
is developed, than on the aplite dike. No attempt was
made to sample only the youngest growth, as new
growth was not obvious. The plant was in bloom at the
time of sampling.

Soil samples were collected at all but three stations.
About 1 pound of soil was collected from 3 inches below
the surface. No true soil profile is developed anywhere
in the area, and existing soil forms only a thin veneer
in protected depressions. The aplite dike, being more
resistant to erosion, stands above the country rock and
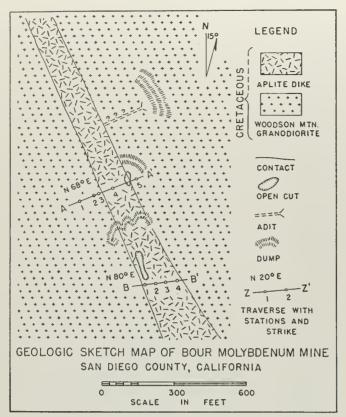is almost devoid of soil.

LEGEND

CRETACEOUS

APLITE DIKE

WOODSON MTN.
GRANODIORITE

CONTACT

OPEN CUT

ADIT

DUMP

N 20° E

Z •——○——○—• Z'
      1   2

TRAVERSE WITH
STATIONS AND
STRIKE

GEOLOGIC SKETCH MAP OF BOUR MOLYBDENUM MINE
SAN DIEGO COUNTY, CALIFORNIA

0   300   600
SCALE   IN   FEET

Figure 6.

Analysis. The plant and soil samples were analyzed in accordance with procedure outlined by Nichols and Rogers (1944). The plants were dried overnight at 100° C., ground in an agate mortar, then ashed in a pot furnace at 450° C. for 2 hours. Silica crucibles were used to avoid salting the samples. Suitable molybdenum standards were prepared with beryllium added as an internal standard, and a working curve was developed. Twenty mg. samples of ash were ignited between carbon electrodes in a D.C. arc using a 4mm. gap at 15 amps. Spectrographs were obtained on a Jarrell-Ash 3.4-meter Wadsworth-mounting grating spectrograph. Line transmission was measured on a Jarrell-Ash micro-photometer, converted to line intensity, and the molybdenum content of the ash obtained to the nearest 10 ppm by comparison with the working curve. The molybdenum line at 3170 Å was used for comparison.

The soil was ground and analyzed in 100 mg. samples in the same manner as outlined for the plants. A determination of soil pH was made in accordance with the method outlined by the Soil Survey Manual of the Department of Agriculture (1951, p. 237). A 1:1 ratio of soil to water was shaken vigorously and allowed to stand for 30 minutes, reshaken and checked with a pH meter. The soil pH was slightly acid in all cases and varied only by one full unit. X-ray analyses determined the principal clay mineral present and the relative amounts in each sample.

Results. The results of plant analysis show a definite anomaly over the metalliferous dike. Background values average 15 ppm molybdenum in the plant ash (Stations

Bour molybdenum mine, San Diego County, California

| | Traverse A-A' | | | | | Traverse B | |
| | Station | | | | | Station | |
	1	2	3	4	5	1	2
Molybdenum concentration in *Cnearidium dumosum* (ppm)	10	20	150	200	10	200	200
Molybdenum concentration in soil	10	20	20	no soil	10	140	no soil
pH of soil	6.00	6.50	6.90	no soil	5.90	6.10	no soil
Relative concentration of illite in soil (percent)	70	100*	60	no soil	90	85	no soil

* Standard (100 percent).

1 and 2, traverse A-A'). At Station 3, which feet from the dike, the concentration reached 15 and at Station 4, near the center of the dike, the denum concentration rose to 200 ppm, falling off to 10 ppm at Station 5, some 50 feet beyond the

The molybdenum concentration in the soil sho similar but weaker anomaly over the ore body. mum concentration was 120 ppm over background imum concentration 10 ppm, in the six soil sample lyzed. On the average the plant samples taken ne ore body contained 100 ppm more molybdenum ash than did the soil samples.

The soil pH ranged from 5.9 to 6.9 and had apparent effect on the molybdenum anomaly. The cipal clay mineral present in the soil was illite. It markedly in concentration; the highest value w corded at Station 2 along traverse A-A' and the trary value recorded at that station was taken standard (100 percent). The lowest concentratio 17 percent of the standard; all other concentration above 50 percent. Like the soil pH, the clay cont the soil had no apparent effect on the anomaly high concentration of molybdenum may have sat the exchange material in the relatively small volu soil, rendering this effect negligible. Howeve slightly acid condition of the soil may have inc the exchange capacity of the illite and lowered t tensity of the anomaly.

Cosumnes Mine

The Cosumnes mine, 15 miles southeast of Place El Dorado County, in section 25, T. 9 N., R. 12 E. is on the Middle Fork of the Cosumnes River i central foothills of the Sierra Nevada.

Mineralization is along the periphery of an ig body which intrudes metasedimentary rocks of the veras group. Molybdenite occurs in minor amou flakes from one millimeter to a centimeter or m greatest diameter. Copper, lead, silver, and gold mi are also found with the molybdenite, which is n northeast-trending quartz vein and contact metam zone.

The oldest rocks in the area are the metasedi of the Carboniferous (?) Calaveras group compos a quartz-biotite-muscovite schist and recrystallized
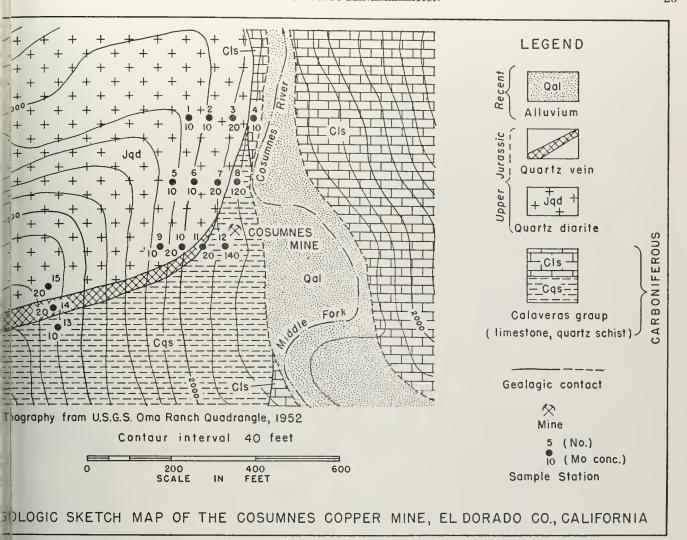
LEGEND

Topography from U.S.G.S. Oma Ranch Quadrangle, 1952

Contour interval 40 feet

0   200   400   600
SCALE   IN   FEET

GEOLOGIC SKETCH MAP OF THE COSUMNES COPPER MINE, EL DORADO CO., CALIFORNIA

FIGURE 7. North is toward top of sketch.

Intrusive into these rocks is a biotite-hornblende diorite of Upper Jurassic age. A contact metamorphic zone is developed along the southwest contact between the quartz diorite and schist. Massive grossularite and epidote are common in this zone. A quartz vein 1 to 15 feet wide follows the igneous-metamorphic contact, and thin veins have invaded the contact zone along minor fractures. Molybdenite was not observed in the quartz vein on the surface, being confined principally to the contact zone.

The mine has been developed along the quartz vein by adits driven from the east and a small open cut at the surface. Two large dumps attest to considerable mine activity.

Geochemistry. Soil samples and leaves and twigs of Interior Live Oak (*Quercus weslenzenii*) were collected at 15 stations in the mine area, and at one station 2 miles distant for a background sample. The samples were located on a grid pattern with the stations spaced 50 feet apart in an east-west direction and 150 feet apart in a generally north-south direction. A short traverse was also made across the quartz vein. An effort was made to collect only young growth, but not current growth,

from trees of approximately the same age. The Interior Live Oak is abundant around the mine and little difficulty was experienced in selecting suitable samples. A deep soil covers the quartz diorite and schist but cover on the limestone is scant and there is none on the quartz vein near the mine. About 1 pound of soil was collected 6 inches below the surface at each station. Eleven of the stations were located on the quartz diorite, three on schist, one each on the limestone and quartz vein. The samples were collected in November 1954.

Analysis. The plant samples were analyzed by a wet chemical technique developed by the U. S. Geological Survey (Reichen and Ward, 1951). Only the leaves were analyzed. The plant material was dried at room temperature for several weeks, then ashed in silica crucibles over a low bunsen flame for 1 hour. A 10 mg. sample of ash was fused with lithium nitrate to destroy the carbonaceous material; the fusion was dissolved in HCl, neutralized, and reacidified. Potassium ferrocyanide and a saturated solution of stannous chloride were added. The solution was shaken with peroxide-free isopropyl ether to abstract the molybdenum complex into the ether layer. Suitable standards of molybdenum were prepared from
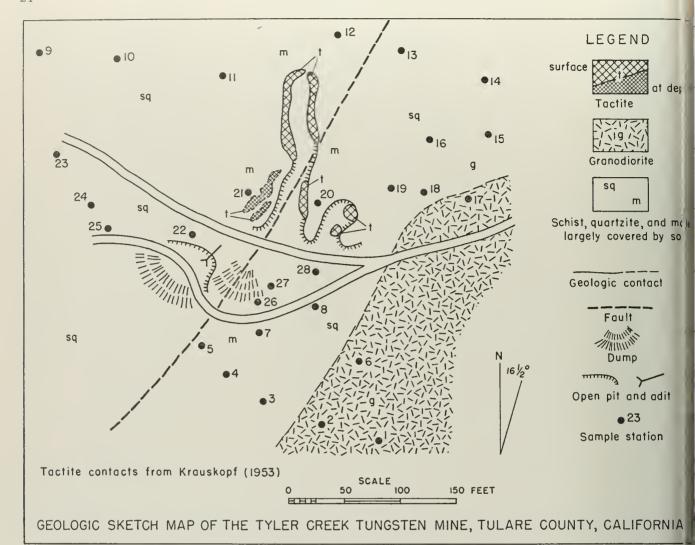
FIGURE 8.

a 0.002 percent molybdenum solution of molybdic oxide. The concentration of molybdenum in the unknown samples was determined to the nearest 10 ppm. by colorimetric comparison with the standards.

The pH of the soil samples was checked in accordance with the procedure outlined by the U. S. Department of Agriculture (Soil Survey Manual, 1951, p. 273).

Results. The concentration of molybdenum in the tree samples increased near the mineralized zone from west to east. Concentration in samples collected over the quartz diorite doubled over the background (10 ppm) while concentration in samples from the schist increased 12 to 14 times over the values recorded on the quartz diorite. There was no significant increase in content in the trees growing on the quartz diorite from north to south. The principal center of molybdenum concentration appears to be in the contact metamorphic zone rather than the quartz vein. This relationship is in keeping with the field observations. A short traverse over the quartz vein, where it was hidden by a deep soil cover several hundred feet west of the mine, showed no anomalous increase in molybdenum.
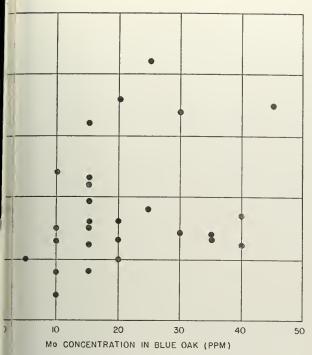
The soil pH was higher in soil samples collecte[d] the quartz diorite than over the other rocks. It r[ ] from 6.25 to 7.00 on the quartz diorite and from [ ] 6.20 on the other rocks.

The pH could not be shown to have a consistent [ ] on the availability of molybdenum to the plant[ ] sample collected on the soil with the lowest pH [ ] contained the highest concentration of molybdenu[m] ppm) which is contrary to what might be exp[ ] Moreover, the second highest molybdenum concent[ ] (120 ppm) was recorded from a tree rooted in soi[l] a pH of 6.20.

Tyler Creek Mine

The Tyler Creek tungsten mine (west workin[g] sec. 35, T. 23 S., R. 30 E., MD., is 2 miles west o[f] fornia Hot Springs, Tulare County, California, [ ] elevation of 3000 feet.

The tungsten mineralization is localized along [a] zone that cuts a roof pendant of schist, quartzit[e] limestone probably of the Kaweah series (Tria[s] and granodiorite (Jurassic ?) country rock (D[ ]

9. Graph showing absence of clear relationship between concentration of molybdenum in Blue oak trees and soil pH.

developed soil, 4 feet deep in some places, covers the greater part of the mine area.

Twig and leaf samples were analyzed in duplicate for molybdenum by the wet chemical technique developed by the U. S. Geological Survey (Reichen and Ward, 1951). The samples were dried at 100° C for 8 hours, then ashed in silica crucibles over a low bunsen flame for 1 hour. The balance of the analysis was carried out as previously described and the results are reported to the nearest 5 ppm.

The soil pH was determined by the U.S. Department of Agriculture method.

Abnormal concentrations of molybdenum were found in 13 of the trees sampled in the mine area. The samples ranged from 5 to 45 ppm molybdenum and averaged 20 ppm.

Table 16. Molybdenum concentration in blue oak growing over different rock types.

	Number of molybdenum samples	Concentration (in ppm)	
		Range	Average
Granodiorite	9	5-40	18
Quartzite and schist	13	10-45	19
Limestone	8	10-35	24

Two background samples taken half a mile and three-quarters of a mile from the mine contained 20 and 10 ppm molybdenum respectively, averaging 15 ppm. The seemingly high (20 ppm) value recorded half a mile from the mine may possibly be explained by the dissemination of tungsten minerals in this region and fortuitous sampling over a mineralized zone.

In general, the highest molybdenum values are rather randomly distributed over the mine area. However, there is some suggestion of a trend northeast from Station 5 to Station 16 with values ranging from 20 to 45 ppm molybdenum. The data are insufficient to explain the high molybdenum content recorded from Stations 1, 9, 16, and 18. Seven stations in the mine area show a content of two to three times the average background (15 ppm). The maximum molybdenum concentrations recorded from this area appear low in view of the high concentrations found in the two previous studies (200 ppm, 140 ppm) all with comparable background values. However, Warren et al. (1953, p. 74) report that of 115 samples collected adjacent to or over ore deposits, 67 tree and plant samples ranged from 2 to 5 ppm molybdenum, and 48 tree samples ranged from 43 to 65 ppm molybdenum; background values were 0.1 to 0.5 ppm. The Blue oak may not be as effective in absorbing molybdenum from the soil as other trees. Analysis of comparative samples (twigs) of Blue oak and California buckeye taken from the same station (5) showed that the California buckeye contained 30 ppm molybdenum as opposed to 20 ppm in the Blue oak.

No significant difference in molybdenum concentration in current and previous years' growth was noted from three stations where both were collected for comparison. The sensitivity of the chemical analysis may not reflect such subtle differences in molybdenum concentration (Reichen and Ward, 1951, p. 1).

; Krauskopf, 1953). Scheelite and powellite are in the pendant along a discontinuous tactite zone strikes generally northeast. The ore is reported average 0.77 percent WO₄ over the mineralized area; samples assayed 29 percent. The scheelite contains admixed powellite in sufficient amounts (probably than 0.4 percent) to draw penalties at the (Jess Acker, lessee, personal communication,

mine has been worked principally along two adits large and two small open cuts. Several dumps to the workings and three unimproved roads considerably disturbed the natural setting. The situated about 150 feet above Deer Creek on a south-sloping hillside.

Geochemistry. Samples of the previous years' of Blue oak (*Quercus douglasii*) twigs were collected at 30 stations and leaves and twigs of California (*Aesculus californica*) were collected at Station Stations 2, 3, and 27 current growth of Blue oak were collected for comparison with the previous growth; at Station 11, leaf samples from the previous years' growth were collected for comparison twigs. Two background samples were collected; one quarter of a mile (Station 29) and another about a mile (Station 30) from the mine, both from trees in soil overlying granodiorite. Samples were from trees of about the same age (1 foot in trunk). The trees were almost devoid of leaves—only from the previous year, and incipient growth from current growing season—were present. The Blue oak uniformly distributed over the mine area. The samples were collected in April 1955.

each of the 30 stations about half a pound of soil collected from 6 inches below the surface. A well-
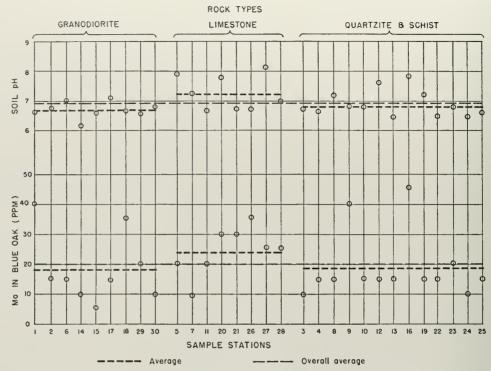
FIGURE 10. Graph showing concentration of molybdenum in Blue oak trees growing in soils of different pH overlying granodiorite, limestone, and quartzite and schist. The parent rock from which the soil is derived affects the soil pH, which in turn affects the amount of molybdenum taken up by the trees.

Table 17. Comparison of new and old growth.

| Station | Molybdenum concentration (in ppm) | |
	Current growth	Previous years' growth
2	15	15
3	15	10
27	20	25

Blue oak twigs and leaves of previous years' growth from Station 11 each contained 20 ppm molybdenum.

The soil ranged in pH from 6.20 to 8.10, averaging 6.90 at 30 stations in the mine area. As might be expected, the soil overlying granodiorite was the most acid; the soil derived from quartzite and schist was intermediate; and limestone soil was the most basic.

The discontinuity of the tactite bodies, the movement of soil by creeping, and the disturbance of the ground by mining operations may account for the lack of any

Table 18. The pH of soil overlying different rock types.

| Rock type | Number of samples | pH | |
		Range	Average
Granodiorite	9	6.21-7.10	6.67
Quartzite and schist	13	6.40-7.75	6.86
Limestone	8	6.65-8.10	7.22

Table 19. Data from biogeochemical survey for moly Tyler Creek mine, Tulare County, California.

Station	Molybdenum content of Blue oak*	Soil pH	Underlying
1	40	6.60	Granodiorite
2	15	6.75	Granodiorite
3	10	6.65	Quartzite and
4	15	6.60	Quartzite and
5	20	7.80	Limestone
6	15	6.95	Granodiorite
7	10	7.20	Limestone
8	15	7.15	Quartzite and
9	40	6.85	Quartzite and
10	15	6.80	Quartzite and
11	20	6.65	Limestone
12	15	7.60	Quartzite and
13	15	6.40	Quartzite and
14	10	6.20	Granodiorite
15	5	6.50	Granodiorite
16	45	7.75	Quartzite and
17	15	7.10	Granodiorite
18	35	6.65	Granodiorite
19	15	7.20	Quartzite and
20	30	7.70	Limestone?
21	30	6.70	Limestone
22	15	6.40	Quartzite and
23	20	6.80	Quartzite and
24	10	6.40	Quartzite and
25	15	6.60	Quartzite and
26	35	6.70	Limestone
27	25	8.10	Limestone?
28	25	6.90	Quartzite and
29[1]	20	6.50	Granodiorite
30[2]	10	6.75	Granodiorite

* Twigs only (in ppm).
[1] Background sample approximately ¼ mi. from mine.
[2] Background sample approximately ½ mi. from mine.

...ite molybdenum concentration pattern in this area. ...ever, as a relatively small area was sampled, it is ...er that the entire mineralized zone is positive for ...lybdenum and that some factors other than the molyb-...num concentration in the soil have partly determined ...molybdenum concentration in the trees.

...ince this study was made, the present operators of ...yler Creek mine have driven an adit N. 60° E. for ...tance of about 300 feet near the former workings. ...helite mineralization was encountered at depth be-...en Stations 20 and 21 where concentrations of 30 ...m molybdenum were found in the plants. At Station ...where the highest molybdenum concentration (45 ...m. was recorded in the plants, an ore body was found ...averaged 0.5 percent WO_3. The total extent of this ...d is not known; however, it has been exposed for ...et in length and 15 feet in width. These discoveries ...r made without knowledge of the biogeochemical ...ic.

SUMMARY AND CONCLUSIONS

...iogeochemical prospecting has not developed to the ...nt where its full potentialities can be realized. If this ...to become a reliable method of prospecting, then cer-...n refinements in application and interpretation are ...cessary.

...t least 19 factors other than the metal concentra-...ion in the soil play an important part in determining ...e metal concentration in plants; at least seven of them ...re controlling factors. These seven are: soil pH, ex-...ange material, other ions, plant type, age of plant and ...gan, translocation, and season.

...The field studies reported here provided a means for ...sting some of these factors. If the effect of one factor ...to be separately evaluated in the field, then areas must ...chosen where the other related factors remain con-...nt.

...The field studies made for this report, made at lo-...lities where, as nearly as possible, four of the seven ...ntrolling factors were constant, showed that the anom-...y detected was due primarily to the high molybdenum ...ncentration in the soil. It was, therefore, a direct ...flection of the underlying ore zone, or was closely ...lated to it. Additional proof that the underlying ore ...posit was the responsible factor was provided by soil ...alyses made from samples taken in the Bour mine ...rea, which showed that the concentration of molyb-...num in the soil fluctuated in the same manner as the ...ncentration of molybdenum in the plants, providing ...arly identical anomalies. The overall concentration in ...e soil, however, was lower than in the plants, showing ...at the plants were a more sensitive prospecting instru-...ent.

...The data collected at the Cosumnes mine showed con-...derable variation in soil pH, and soil ions, which may ...ave been due to the three underlying rock types. The ...erage soil pH was definitely higher over the quartz ...dote than over the metamorphic rocks. However, this ...ctor had little apparent influence on the metal con-...nt of the plants as the highest molybdenum values were ...corded from soils with the lowest pH. Molybdenum ...ncentration increased as the ore zone was approached ...cept at one station where there is some evidence that

the suppressing effect of CO_3 and HCO_3 ions, derived from the underlying limestone, reduced the uptake of molybdenum. As at the Bour mine, the high concentration of molybdenum in the soil had a greater effect on the metal concentration in the plants than did the other controlling factors.

More than half of the plant samples collected at the Tyler Creek mine showed no anomalous concentration of molybdenum and there was no uniform concentration pattern related to the ore zone. The data point to the underlying rock type as a principal influence in regulating the soil pH; therefore the rock type might be expected to have some influence on molybdenum concentration in plants. Unfortunately, the data here are insufficient to demonstrate such an influence conclusively. Nevertheless, it will probably be necessary in future investigations to apply a correction factor when traversing from one rock type to another. The anomalous molybdenum content of the plants was considerably lower in the Tyler Creek mine area than at the other two mine areas studied. This may have been due in part to the molybdenum concentration in the soil although, in view of the rather erratic results, it seems likely that the plant type sampled or the high concentration of CO_3 and HCO_3 ions in the soil at certain stations may have reduced the assimilation of molybdenum by the plant. This area then illustrates to a limited degree how the other factors can obscure and disperse a biogeochemical anomaly. The fact that most of the plant samples show a greater than normal molybdenum concentration is evidence that the soil molybdenum concentration is still the principal controlling factor in this area.

Future work in biogeochemistry should be directed toward the accumulation of data on plant-metal-soil relationships for all of the economic metals. The character of the metal as it is related to the soil chemistry and to the geology appears more vital than the influence exerted by the plant. It is true that certain physiological features of plants exert a significant influence in biogeochemistry, but on the whole all plants react with a certain degree of consistency. The important controls lie in the soil chemistry. The behavior of molybdenum is not yet completely understood and there is a real need to extend the studies begun in this investigation. The influence of all the important rock types on molybdenum anomalies would be of interest as would the effect of a wider range in soil pH. More study should be given to the geologic controls. Molybdenum-plant relationships in the vicinity of ore deposits should also be tested under a greater range of climatic conditions.

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